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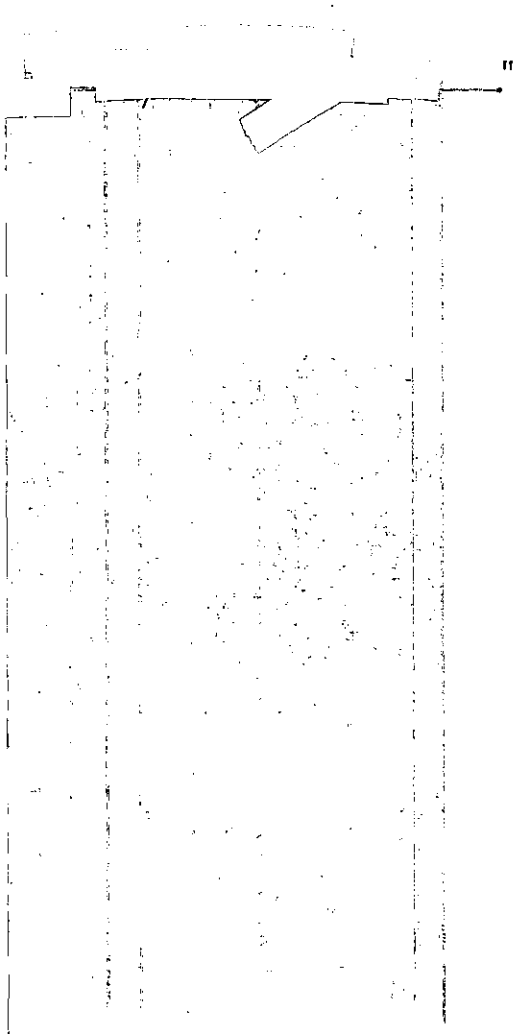

THE CATALYTIC HYDROGENATION OF SOME TALL OIL CONSTITUENTS

A THESIS

Presented to

the Faculty of the Graduate Division

by

Ronald Goldin Jones

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

in the School of Chemistry

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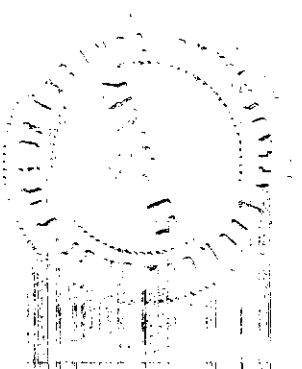

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Approved:

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SUMMARY

The purpose of this research was to determine the reaction rate constants for the hydrogenation of several tall oil fractions and for the hydrogenation of oleic acid and abietic acid, the principal fatty acid and resin acid components of tall oil. The effect of several reaction variables upon the rate constants were investigated, as well as the values for the activation energies for the most important fractions.

The hydrogenation reactions were carried out at approximately room temperature, in a standard Parr Low Pressure Reaction Apparatus having a total volume of 4.48 liters. The solvent used for most of the reactions was distilled glacial acetic acid, and the catalyst was Adams' platinum oxide. Most of the reductions were carried out at a starting hydrogen pressure of approximately 64.7 p.s.i. aboslute. It was found that the reaction rate constants could be determined by following the drop in hydrogen pressure during the reaction as a function of the time elapsed during the reduction. The reactions were found to obey first order kinetics with respect to hydrogen.

Four tall oil fractions manufactured by the Arizona Chemical Company, 30 Rockefeller Plaza, New York 20, N. Y. were studied. These fractions are known by the commercial names of Acintol D, Acintol FA 1, Acintol FA 2, and Acintol P. All of these fractions originate from the fractional distillation of crude tall oil. Acintol FA 1 consists primarily of fatty acids; its repeated fractionation results in Acintol FA 2. Acintol D is an intermediate fraction consisting of both fatty acid and

resin acid components, while Acintol P is a mixture of materials which have very high boiling points and is the residue from the first distillation of crude tall oil.

In addition to the above materials, a tall oil fraction rich in resin acids was investigated. This fraction is called commercially Tall Oil Rosin and is produced by the West Virginia Pulp and Paper Company, 230 Park Avenue, New York 17, N. Y. This fraction was also used as the source from which abietic acid and diamylammonium abietate were obtained. These materials were investigated as well as oleic acid and methyl oleate.

The hydrogenation of six grams of Acintol FA 1 and of Acintol FA 2 in 100 ml. of glacial acetic acid solvent with 0.10 g. of Adams' platinum oxide catalyst was found to yield very similar data. The reaction rate constants in these cases were found to be approximately 0.210 $min.^{-1}/g.$ at a temperature of 25°C. Acintol FA 2 under similar conditions except using 0.16 g. of Adams' platinum oxide yielded a rate constant value of 0.145 $min.^{-1}/g.$ Acintol FA 2 was shown to yield stearic acid as the product of the hydrogenation.

Hydrogenation of Acintol D under conditions as described above using 0.10 g. Adams' platinum oxide catalyst yielded a rate constant value of 0.234 $min.^{-1}/g.$

The hydrogenation of Acintol P was found not to be favorable under the same conditions as used in the other Acintols. Several treatments of the Acintol P were attempted in an effort to cause the hydrogenation to proceed but without very much success. It was found, however, that the acidic components of Acintol P could be extracted from the parent material by the action of glacial acetic acid, and that they were able to be

hydrogenated. Reaction rate constant data were not obtainable for these materials.

The hydrogenation of 6.00 g. of Tall Oil Rosin in 100 ml. of distilled glacial acetic acid solution with 0.40 g. of Adams' platinum oxide catalyst was found to proceed much slower than that of the fatty acid fractions. The reaction rate constant was found to be 0.0453 $min.^{-1}/g.$ at 25°C.

Oleic acid and methyl oleate were found to yield similar rate constants when 0.02 mole of these materials were hydrogenated in 100 ml. of glacial acetic acid solution with 0.10 g. Adams' platinum oxide. The values derived were 0.190 $min.^{-1}/g.$ and 0.110 $min.^{-1}/g.$ respectively at a reaction temperature of 25°C.

The hydrogenation of abietic acid was studied by using either the free acid in acetic acid as solvent or the diamylamine salt of the acid in acetic acid solution. The latter was expected to parallel the former in results, since in a large excess of acetic acid, the salt would be expected to be converted into abietic acid, and diamylammonium acetate. This was the case and both materials yielded initial reaction rate constants of 0.0350 $min.^{-1}/g.$ at a temperature of 25°C.

The hydrogenation of abietic acid was found to proceed through a two step progression. This was characterized by an initial rapid uptake of hydrogen, followed by a slower transition phase which did not follow first order kinetics, and by a third slow reaction which was again first order with respect to hydrogen. It was found to be difficult to reproduce the rate constant values obtained for the third phase of the reduction, but they were approximately 0.0010 $min.^{-1}/g.$

On the basis of this information and other experiments carried out during the course of this work, it is believed that the hydrogenation proceeds through the reduction of abietic acid to a dihydroabietic acid, the structure of which is unknown. This half-hydrogenated abietic acid is believed to undergo subsequent hydrogenation to afford a tetrahydroabietic acid, the stereochemistry of which is also unknown. The hydrogenation of a 7,8-dihydroabietic acid under identical conditions yields a rate constant value intermediate to the ones obtained for the first and third phases of the reduction of abietic acid.

The apparent activation energies were determined for the hydrogenation of Acintol FA 2, methyl oleate, and diamylammonium abietate. The values obtained are 3.51 kcal./mole, 4.52 kcal./mole, and 5.35 kcal./mole, respectively. While the hydrogenation of Acintol FA 2 and oleic acid were shown to produce stearic acid, the products from the half hydrogenation or complete hydrogenation of abietic acid were not characterized. This was not achieved, since suitable conditions which permitted the separation of the mixtures of products formed in these reactions were not found.

CHAPTER I

INTRODUCTION

Since the purpose of this research was to conduct a study of the hydrogenation of tall oil and some of its constituents, it would be well to consider first not only the origin and composition of tall oil but also something of the theory of heterogeneous catalysis.

The field of heterogeneous catalysis for many years was little more than an art. As reports of the utilization of this art expanded in number and techniques began to be more standardized, so that data could be compared, the art acquired more and more of the characteristics of a science. While much work has been done in an effort to further the understanding of this field as a science, it still remains in its infancy. At this time, there is no single theory which explains all heterogeneous catalytic phenomena, but there is a qualitative understanding of the processes. Emmett (1) has edited a series of volumes which give detailed consideration to the subject of catalysis, and this source should be consulted for a more comprehensive discussion of the theories and practices of heterogeneous catalysis.

In order to explain what may occur in the various processes that lead to chemical reaction *via* heterogeneous catalysis, some understanding of the action taken by the catalyst must be had. It is obvious that something very important must occur at the catalyst surface, since reactions

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(1) P. Emmett, *Catalysis*, Vols. I-VII, Reinhold Publishing Corp., New York, N. Y., 1954-1960.

which do not appear to proceed at an appreciable rate in the absence of catalysts may be caused to produce excellent yields of products by the presence of a suitable catalyst. It then seems reasonable that an interaction of the reactant molecules must occur at the catalyst surface and that this interaction energetically favors the formation of the product.

The most generally accepted explanation of the interaction which results in production of the product in heterogeneous catalytic systems is based upon the theory that one or more of the reacting molecules are adsorbed upon the catalyst surface. Adsorption is a process in which the molecules of one material become concentrated upon the surface of another. This can occur between a gas and a liquid, between two immiscible liquids, between a gas and a solid, between a liquid and a solid, and between the components of a solution and a solid. In catalytic hydrogenations the adsorption frequently occurs between the components of a solution and a solid. It has been shown that two different kinds of adsorption occur. These are known as physical adsorption and chemisorption.

Physical adsorption arises because of physical forces which attract the two involved materials and maintain them at some relatively small and constant distance from each other. These forces correspond to van der Waals forces and this type of adsorption is referred to as van der Waals adsorption. As might be expected on the basis of the relationship between the physical adsorption forces and van der Waals forces, the heat evolved during the occurrence of physical adsorption of a gas on a solid surface is usually very nearly the same as the heat of liquefaction of the gas. This is frequently found to be only a few hundred

calories per mole. Therefore, physical adsorption is thought to have no great importance in connection with heterogeneous catalytic reactions.

Chemisorption derives its name from the chemical bond-like forces which are characteristic during its occurrence. The heat evolved in this process varies from ten to one hundred kilocalories per mole depending upon the interacting materials. This is of the same order of magnitude as the heat of conventional chemical bond formation. This suggests that chemical bonding forces are responsible for maintaining the adsorbed molecules at some small distance from the catalyst surface. Furthermore, it is implied that the adsorbed material is greatly changed chemically. The chemical reactivity could be greatly increased to give rise to a favorable reaction condition or could be greatly decreased which would correspond to a case of catalyst poisoning. Langmuir (2) predicted that chemisorption could give rise to only unimolecular layers of adsorbed material on surfaces of another phase. This has been demonstrated by Roberts (3) who found that the number of hydrogen atoms adsorbed upon a tungsten surface was very nearly equal to the number of tungsten atoms available.

In heterogeneous catalysis like in other reaction systems, the rate of the reaction which occurs is determined by a series of steps. One of these steps is significantly slower than the others and is termed the rate controlling step or the slow step. It is the rate of this step which is measured when the rate of the reaction is measured. In the case of catalytic hydrogenation, there are several steps or occurrences

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(2) I. Langmuir, J. Am. Chem. Soc., 38, 221 (1916).

(3) J. Roberts, Proc. Royal Soc., A152, 445 (1935).

which must come about before the overall reaction takes place or is considered complete. First, it is necessary that the reactants reach the vicinity of the catalyst surface. It is next required that one or more of them become adsorbed upon the catalyst so that the correct geometry or a favorable energetic situation exists to permit the reaction to occur. It is then necessary that the reactants undergo the reaction or combine in hydrogenation reactions. Finally, in order to permit the continuation of the reaction, the product molecule formed in this combination must be desorbed from the catalyst surface, enabling subsequent use of the surface by other reactant molecules.

In the first of these requirements, a material which is to be hydrogenated in solution in the presence of the catalyst must come near the catalyst surface by the movement of its dissolved molecules through the solution. The same is true for gaseous hydrogen dissolved in the solvent. That is to say, the reactants must diffuse through the solution until they reach the catalyst surface. It is frequently found that the rate of the reaction will not be dependent upon the concentration of acceptor, so long as sufficient acceptor is available to cover the reaction sites of the catalyst surface. Similarly, the relative concentration of hydrogen should not vary greatly during a hydrogenation reaction, since usually the pressure change is not very great. Therefore, the solubility of the gas in the solvent should not vary greatly. It is commonly found, however, that hydrogenation reactions are kinetically first order with respect to hydrogen. Vigorous agitation of a hydrogenation solution in the presence of the catalyst during the processing of the reaction minimizes the occurrence of any differences in diffusion rates.

The second requirement, that the reactants must be adsorbed, could

take several courses depending upon the nature of the catalyst and substrate. In some cases the hydrogen adsorption might be the rate controlling step, while in others the adsorption of the substrate could be the rate controlling step. It has been suggested that the hydrogenation reaction could occur after both hydrogen and acceptor were adsorbed on adjacent sites, and also that reaction might occur after only one of the reactants had been adsorbed and the second in the solution had come near enough to the first to permit combination. It is known, for example, that a catalyst surface may become saturated in one reactant, and the reaction rate constant may be affected by this.[1]

With regard to the third requirement, it has been postulated that one or the other reactants may be adsorbed, and then in its activated state reacts with the other. Another suggestion is that the two reactants are both adsorbed on adjacent catalyst sites before reaction occurs. Still another possibility is that the two reactants may become adsorbed on the catalyst surface and then may have two degrees of translational freedom so that their movement on the catalyst could result in their occupying adjacent sites followed by the occurrence of the reaction. It is conceivable that any of these processes could operate in a given reaction, and furthermore, that the mechanism could change as the conditions of the reaction were changed.

The energy of activation of hydrogenation reactions may be determined by following the change in the reaction rate constant resulting from changes in the temperature at which the reaction is conducted. Since

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[1] See below, page 47.

several of the occurrences in a hydrogenation reaction have energies of activation, the observed energy is only an apparent energy of activation. If the mechanism of a hydrogenation reaction varies with temperature, then it may be found that the apparent energy of activation varies also. There are at least three of the steps which have activation energies of significant magnitude. These are the adsorption steps, the reaction step, and the desorption step.

The last requirement that the product of the hydrogenation reaction must be desorbed is necessary to the continuation of the reaction. It is necessary that the product not only be desorbed, but also diffuse away from the catalyst surface to provide accessibility to the surface of other reactant molecules. Again, variations in the rate of diffusion of the product are minimized by keeping the hydrogenation solution in constant motion. If the product is very rapidly desorbed, then this favors some other step in the reaction sequence being the rate determing step. On the other hand, if the product is desorbed only slowly, then it may be the rate determining step. In some cases, it is found that the product is desorbed with great difficulty which results in poisoning of the catalyst surface. poisoning is more frequently caused by some impurity which is readily adsorbed being present in the reaction solution. The impurity occupies reaction sites on the catalyst to the exclusion of the desired reactants and is desorbed very slowly.

Before consideration of the hydrogenation of tall oil, a brief discussion of its origin would be helpful to the understanding of this topic. In the paper industry, the soda and sulfate processes are used for the conversion of wood pulp containing cellulose and other carbohydrates,

lignin, resins, and fats into a paper-making pulp which contains a much higher percentage of cellulose than the starting material. In both of these industrial procedures, the wood pulp is digested at high temperatures with a mixture of alkali and sulfide. The cooking process changes the undesirable constituents of the wood pulp into water soluble materials which can be washed out of the pulp. The dark solution which results is known as black liquor and is concentrated by evaporation of some of the water. After concentration, the solution is allowed to cool to produce a mixture of fatty acid and resin acid soaps which separate as a brown curdy mass known as black liquor soap. This material is skimmed off, and after boiling with sulfuric acid solution to convert the sodium soaps into the free acids, followed by cooling, a brown oil separates from the solution. This oil is commonly known as tall oil, and for many years was discarded as worthless. In recent years, particularly since the beginning of World War II, this mixture of organic chemicals has been recognized as a valuable source of fatty acids and rosins which can be used to advantage in the manufacture of linoleum, soaps, degreasing compounds, disinfectants, paints and varnishes, gloss oils, esters, and cutting oils.

The composition of tall oil varies depending upon the processes used in its isolation, the species of the wood from which it was derived, and the geographic location in which the wood was grown. Generally, it is found that tall oil will contain approximately 45 per cent fatty acids, approximately 45 per cent resin acids, and approximately 10 per cent unsaponifiable materials. The principal fatty acid is oleic acid and comprises about 50 per cent of the total fatty acid content. The

conjugated linoleic acid and unconjugated linoleic acid account for about 40 per cent of the total fatty acids present, with the remaining 10 per cent consisting of saturated fatty acids. Harris (4) has estimated the composition of the resin acid portion of tall oil to be approximately 30 to 40 per cent abietic acid, approximately 10 to 20 per cent neoabietic, approximately 14 per cent each of dihydroabietic and tetrahydroabietic acids, with small percentages of dehydroabietic acid, dextropimaric acid, and isodextropimaric acid constituting the remainder of the mixture. The unsaponifiable materials are present in only comparatively minor amounts and consist mainly of terpenic hydrocarbons, long-chain alcohols, and sterols.

Through the technique of fractional distillation, tall oil has been separated into fractions which are rich in either fatty acids or resin acids. This has resulted in improvements in the application of this source of raw materials. In order to improve the aging characteristics, change the physical properties, and extend the use of tall oil, it is frequently catalytically hydrogenated. From an industrial standpoint, this process has received considerable interest. Many patents have been issued and articles written on the subject of hydrogenation of tall oil. All of the data available as a result of this have served to aid the industry in improving its products; but little if anything has been done which extends the understanding of the fundamental chemical changes which occur in this process. Studies of the kinetic behavior of the hydrogenation reactions have not been conducted, and it appears that only qualitative knowledge about the reaction is available.

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(4) G. Harris, TAPPI Monograph Series No. 6, 167 (1948).

The hydrogenation of tall oil has been exploited industrially, and the literature abounds with inventions involving this process. Catalysts and conditions have varied considerably as well as the nature of the products derived from the procedures. Weiner (5) has compiled a bibliography of the tall oil literature covering that available through the end of 1957.

Perhaps one of the most significant pieces of information on the hydrogenation of tall oil provided by the literature is that the fatty acid constituents reportedly hydrogenated preferentially to the resin acids (6). It might be presupposed that this would necessarily indicate that the fatty acids of tall oil hydrogenated at a greater rate than the resin acids. This conclusion, however, cannot be made on the basis of preferrential hydrogenation alone. This is illustrated through the example of the hydrogenation of 3-ethyl-2-pentene and 1,1-diphenyl-1-propene. In the hydrogenation of these materials on a platinum surface, the first compound was found to be more active than the second compound, and in admixture it was hydrogenated preferentially. If palladium or Raney nickel was used as the catalyst, the reactivity would not be changed, but the second compound is known to hydrogenated preferentially to the first (7).

It is interesting to note that due to the more difficult hydro-

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(5) J. Weiner, Tall Oil, Bibliographic Series Nos. 133-135, The Institute of Paper Chemistry, Appleton, Wisconsin, 1959.

(6) A. Turck and J. Ross, U. S. Patent, 2,389.284 (Nov. 20, 1945), C.A., 40, 1657 (1946).

(7) B. Corson in Catalysis, Vol. III, Edited by P. Emmett, Reinhold Publishing Corporation, New York, N. Y., 1956, p. 82.

genation of the resin acids present in tall oil, the products are rendered less stable to discoloration than would be desired. This has been improved upon by first treating tall oil with a catalyst which would effect the disproportionation of abietic acid into dihydroabietic acid, tetrahydroabietic acid, and dehydroabietic acid, before hydrogenating the tall oil. This renders tall oil less difficult to hydrogenate and increases the stability of the product (8).

Hydrogenation of the fatty acids of tall oil would be expected to produce stearic acid as the product, since the unsaturated acids all possess straight chains containing eighteen carbon atoms. The hydrogenation of these individual acids has been studied extensively with regard to conditions and catalysts which are suitable for the reaction. The literature on this subject is too extensive for consideration herein.

The resin acid constituents have not received as much attention with regard to their hydrogenation as have the fatty acids. The hydrogenation of abietic acid has been investigated by several workers. One of the earlier reports of the hydrogenation of this material was by Ruzicka and Meyer (9) who found that a dihydroabietic acid melting at 167-168° and having a specific rotation of -12° was obtained when platinum black was used as catalyst in alcohol. These workers claimed that the utilization of platinum in acetic acid solution caused the hydrogenation of abietic acid to yield a mixture of dihydroabietic acid and tetrahydroabietic acid which melted at 140-142°. A more active platinum catalyst

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(8) R. Dressler, R. Vivian, and T. Hasselstrom, U. S. Patent, 2,371,230 (March 13, 1945), C. A., 39, 3431 (1945).

(9) L. Ruzicka, and J. Meyer, Helv. Chim. Acta, 5, 315 (1922).

was found to cause the starting acid to be converted completely into a tetrahydroabietic acid, melting at 137-139°.

Other workers (10) have found that reduction using palladium on calcium carbonate gives a dihydroabietic acid melting at 166-168° but having a positive specific rotation of +10.3°.

Palladium catalyst on carbon has been investigated for the hydrogenation of abietic acid at high pressure and was found to transform the substrate into a dihydroabietic acid which melts at 175° and has a specific rotation of +123° (11). It was also reported that when platinum was used in alcohol solution, abietic acid was transformed into a dihydroabietic acid which melted at 166° and had a specific rotation of -26°. This appears to be identical to the material obtained by Ruzicka and Meyer using similar conditions as noted above.

Most recently, Lombard (12) reported that hydrogenation of abietic acid with nickel catalyst at room temperature yields a dihydroabietic acid melting at 143° and having a specific rotation of +40°. The same catalyst in ethanol at 130° is said to convert the parent acid into a tetrahydroabietic acid.

All of these reports are without conclusive evidence for the structures of the products obtained. The physical constants vary considerably from the report of one group of workers to that of another. It appears that the only dihydroabietic acid which is very well characterized is

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(10) L. Ruzicka and S. Kaufmann, Ibid., 24, 1389 (1941).

(11) R. Lombard, Bull. Soc. Chim., 11, 526 (1944).

(12) Loc. cit.

that reported by Royals (13). Reduction of abietic acid with lithium metal in liquid ammonia yielded a 7,8-dihydroabietic acid the stereochemistry of which is unknown.

The products which have been observed as results of hydrogenation experiments are undoubtedly mixtures and apparently have not been accurately characterized. If one assumes the nonisomerization of the double bonds of abietic acid and of any intermediate dihydroabietic acid during the full hydrogenation of the parent acid, there would be four tetrahydroabietic acid isomers theoretically possible. Isomerization of the double bonds could lead to a larger number of possibilities. There appears to have been no effort to characterize the reported tetrahydroabietic acids.

It has been the purpose of this research to determine the kinetics of the hydrogenation reactions of several typical tall oil fractions, rich either in fatty acids or in resin acids. It also was desired to determine the effect upon the rate constant values of several of the variables in the reactions, such as amount of catalyst, amount of hydrogen acceptor, temperature, and nature of solvents. It also was intended to conduct a similar study on the hydrogenation of abietic acid and oleic acid. As has been pointed out, these compounds are, respectively, the principal resin acid and fatty acid components of tall oil.

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(13) E. Royals, W. Bailey, and R. Kennedy, J. Org. Chem., 23, 151 (1958).

CHAPTER II

DISCUSSION OF EXPERIMENTAL RESULTS

Results of the Hydrogenation of Tall Oil Fractions

The study of the hydrogenation of tall oil has been confined principally to a series of fractions supplied by the Arizona Chemical Company and designated by the commercial name "Acintols". Four different Acintols or tall oil fractions were used in the hydrogenation experiments, and the commercial specifications of these materials are given in Table 1.

Table 1. Typical Lot Specifications of Acintols

	Acintol FA 1	Acintol FA 2	Acintol D	Acintol P
Color (Gardner)	8	6+	8	17
Acid Number	191	194	190	50
Saponification Number	194	196	193	110
Iodine Number (Wijs)	138	129	164	138
Resin Acids %	4.0	1.3	29	31
Unsaponifiables %	4.0	1.8	1.5	33
Fatty Acids %	92	97	69	33
Specific Gravity	0.9005	0.8999	0.9465	1.010

Hydrogenation of Acintols

Acintol FA 1.--Acintol FA 1 contains approximately 92 per cent fatty acids which consist of 4 per cent saturated acids, 7 per cent linoleic acid ($\Delta^{9,11}$), 39 per cent linoleic acid ($\Delta^{9,12}$), and 50 per cent oleic

acid. There is also present a small amount of unsaturated resin acids and unsaponifiables. Samples of 6.00 g. of this material were hydrogenated in 100 ml. of glacial acetic acid using Adams' platinum catalyst. The results are tabulated in Table 2.

Table 2. Hydrogenation of Acintol FA 1

Run Number	Catalyst: Lot	Weight, g.	Mean Temperature °C	k x 10^4 $min.^{-1}/g.$*
1	A	0.10	32.3	2153
2	A	0.10	33.6	2246
3	A	0.10	33.4	1844

*Rate constants are corrected to 25°C and to catalyst lot C.

After removal of the catalyst by filtration, the product was isolated by crystallization from the heated solution of the reaction mixture. The product was recrystallized from ethanol and dried. The crystals so obtained were found to have a melting point of 69.4-70.4°C. The principal product of the hydrogenation of Acintol FA 1 is stearic acid, and further characterization of the crystals was not attempted.

Since Acintol FA 1 and Acintol FA 2 were quite similar materials, a detailed study of the hydrogenation of each of these fractions was not carried out. Acintol FA 2 was chosen as the fraction for the more detailed study because of its slightly simpler composition.

Acintol FA 2.--Table 1 shows Acintol FA 2 is 97 per cent fatty acids. Of this only 2 per cent is saturated compounds, 6 per cent is linoleic ($\Delta^{9,11}$), 42 per cent is linoleic ($\Delta^{9,12}$), and 50 per cent is oleic acid.

Hydrogenation in glacial acetic acid.--Most of the hydrogenations of Acintol FA 2 used 6.00 g. of the acceptor in 100 ml. of glacial acetic acid with Adams' catalyst. Several runs were carried out using different weights of catalyst. The results are listed in Table 3 and are illustrated graphically in Figure 1, page 16.

Table 3. Hydrogenation of Acintol FA 2

Run Number	Catalyst: Lot	Weight, g.	Mean Temperature °C	$kx10^4/min.^{-1}/g.$*
1	C	0.0146	28.3	1933
2	C	0.0203	28.3	3763
3	C	0.0316	28.3	3106
4	C	0.0416	28.3	3210
5	A	0.0500	33.0	3540
6	A	0.0500	33.0	3411
7	A	0.0500	33.0	2897
8	C	0.0506	27.3	2986
9	C	0.0605	27.3	2947
10	C	0.0721	27.3	2796
11	C	0.0791	29.0	2463
12	C	0.0901	29.0	2203
13	A	0.1000	31.3	2110
14	A	0.1000	31.4	2088
15	A	0.1000	31.6	2078
16	C	0.1045	29.0	2193
17	C	0.1119	28.9	1803
18	C	0.1318	28.9	1604
19	A	0.1500	34.0	1493
20	C	0.1612	29.2	1450
21	C	0.1970	29.6	1227
22	C	0.2170	29.2	1073
23	C	0.2990	29.0	876

*Rate constants are corrected to 25°C and to catalyst lot C.

The rate constants were obtained by plotting values for log P_o/P_t as ordinates against values for time as absicissas.[1] From the slope of

[1]See below, page 87 .

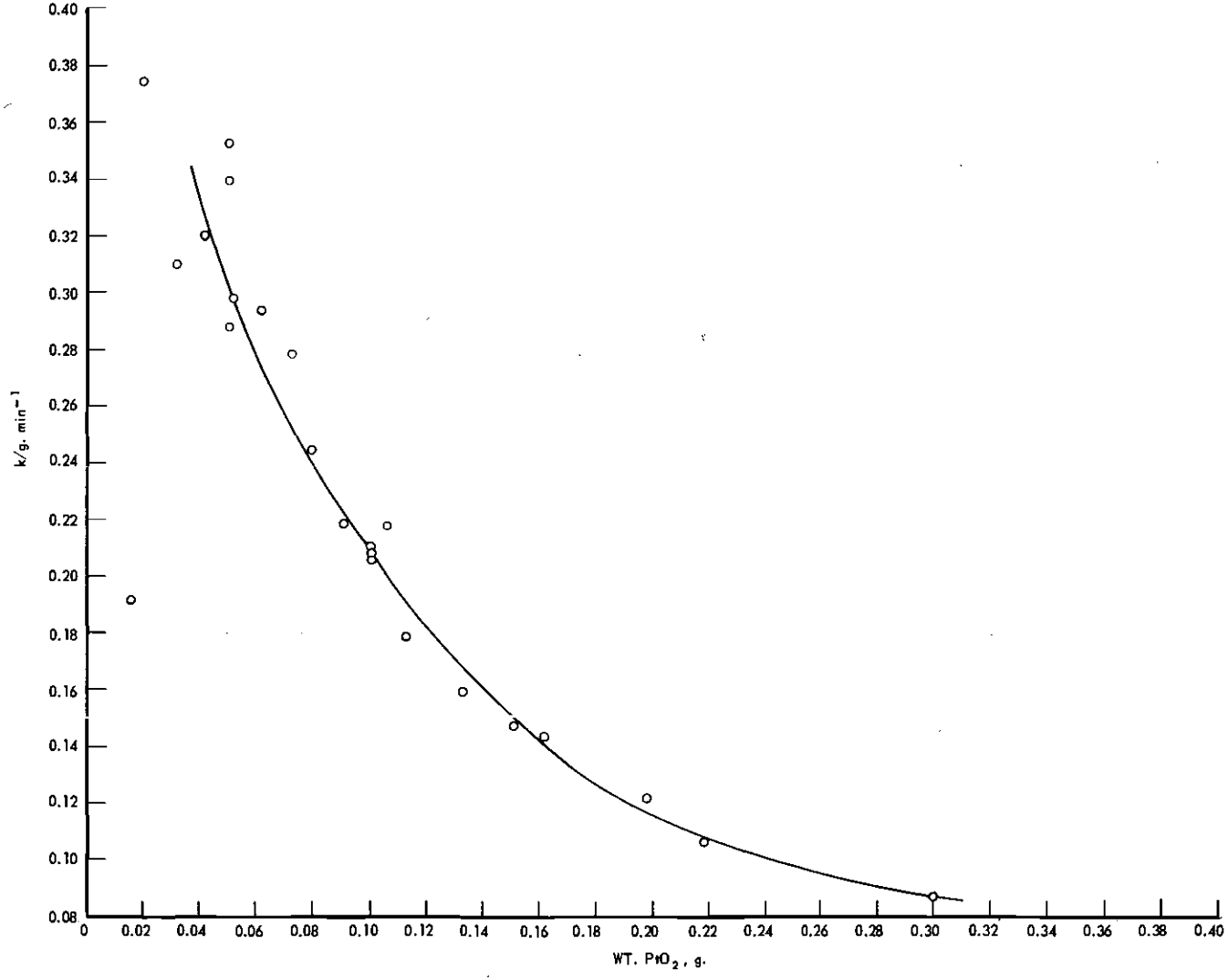

Figure 1. Rate Constant Per Gram of Catalyst Against Weight Catalyst.

the straight line obtained, the rate constant was calculated. In most cases, the slope of the line could be quite easily drawn, but when very small amounts of catalyst were used, the plotted data did not fit a straight line as well as was desired. This could be due to two factors. When small amounts of the surface become poisoned, the percentage of available catalyst surface has been greatly decreased. On the other hand, errors in weighing the catalyst sample would be much greater per unit of weight in this case than would be encountered when using a large weight of catalyst. Rather poor reproducibility in the rate constants resulted from this overall effect as is shown by runs 5, 6, and 7 in Table 3. Deviations in the rate constants obtained from these plots were as great as 8 per cent. On the other hand, deviations of less than 1 per cent were not uncommon (see runs 13, 14, and 15, Table 3).

The variation of the rate constant per gram of catalyst in the case of the hydrogenation of Acintol FA 2 is not uncommon. Usually, it is found that a plot of data similar to that shown in Table 3 for other hydrogenations will yield a curve as is illustrated in Figure 2, page 18.

This figure may be understood by considering qualitatively what occurs in the hydrogenation reaction. In order for the catalytic reaction to occur, basically, the following things must take place:

1. Hydrogen must reach and be adsorbed on the catalyst surface.

2. The substrate must reach and be adsorbed on the catalyst surface.

3. The substrate and hydrogen which are adsorbed on the surface must undergo reaction to yield the hydrogenated product which is still adsorbed on the catalyst.

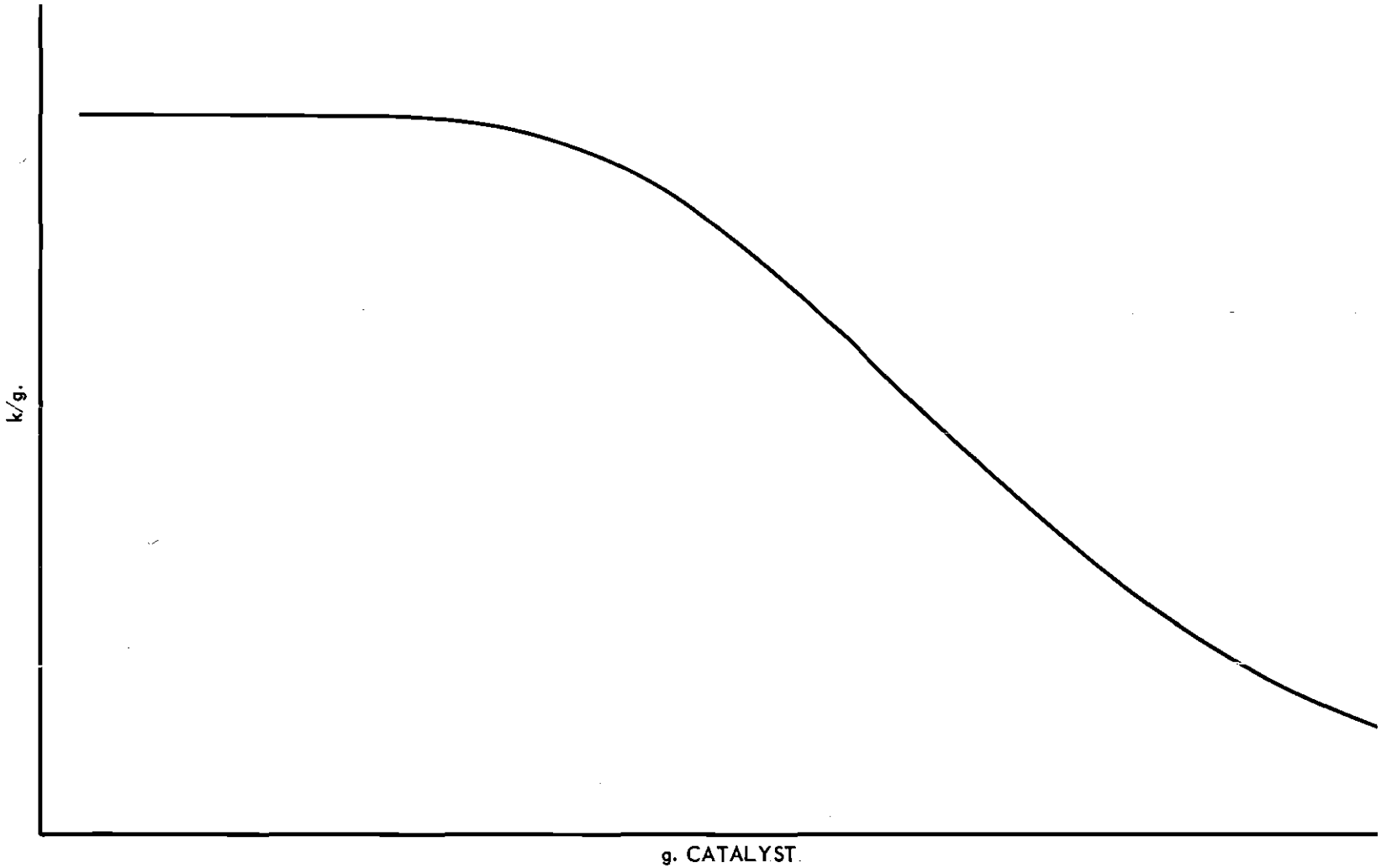

Figure 2. Typical Variation in Rate Constant Per Gram of Catalyst with Varying Weight Catalyst.

4. The hydrogenated product must be desorbed from the catalyst surface.

In Figure 2, the part of the curve which is straight and parallel to the catalyst weight axis represents a range of catalyst weight to acceptor weight wherein the rate is directly proportional to the weight of catalyst. That portion of the curve for larger weights of catalyst represents a range of catalyst weight to acceptor weight wherein the rate constant is no longer directly proportional to the weight of catalyst. Under a condition such as this, all of the available catalyst surface is not being used to its maximum capacity. Here the reaction would occur, and the product would be desorbed, and rather than more reactants being immediately adsorbed so that reaction could occur, the catalyst surface would be left to await the approach of acceptor and/or hydrogen molecules. This is responsible for that part of the curve in Figure 2 which seems to indicate that the value of k decreases with increaing catalyst weight. The figure is constructed by plotting k/g. against catalyst weight, however, and since the value for k would approach a limiting factor as described above, then k/g. would decrease as larger amounts of catalyst were used.

Figure 1 shows that a range of catalyst weights was not found in which the rate of hydrogenation for Acintol FA 2 was directly proportional to the catalyst weight. It would have been desirable to also have data in the weight range of 0.00 g. to 0.02 g., but the extremely small amount of catalyst used in such runs produces straight lines only for the very first part of the rate constant plot, indicating that at low amounts of catalyst, poisoning effects become significant.[1]

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[1] See above, page 17 .

It would have been desirable to have measured the rate constant at higher weights of catalyst than 0.30 g., but even at this weight of catalyst the rate of the reaction was so fast that the reaction was complete after only one and one half minutes. This necessitated making readings of pressure every fifteen seconds on a gauge calibrated in such a manner that values to the nearest 0.05 p.s.i. were the best obtainable. To complicate the problem further, the total drop in pressure was only about 2.75 p.s.i. For these reasons, the weight of 0.16 g. was selected as a convenient catalyst weight to be used in other studies in the hydrogenation of Acintol FA 2.

In addition to the above information, the dependence of the rate constant upon the amount of acceptor present in the reaction solution was very briefly investigated. Results shown in Table 4 indicate the rate is independent of the concentration of Acintol FA 2.

Table 4. Hydrogenation of Acintol FA 2 in 100 ml. of Glacial Acetic Acid with 0.10 g. of Catalyst Lot A

Run Number	Weight of Acceptor g.	Mean Temperature °C	Rate Constant* $\times 10^4$ $min.^{-1}/g.$
13	6.00	31.3	2110
14	6.00	31.4	2088
15	6.00	31.6	2078
24	3.00	34.9	1941

*Rate constants are corrected to 25°C and to catalyst lot C.

This table shows that there is no significant change in the rate constant even though the concentration of acceptor varied two fold.

It would seem appropriate at this point to call attention to the fact that the data obtained in the hydrogenation of Acintol FA 1 very closely parallel the above data. The average rate constant, corrected to 25°C and to catalyst lot C, times 10^{-4} $min.^{-1}/g.$ for the three runs given in Table 2 is 2061. This is very nearly the same as the value of 2092, the average of runs 13, 14, and 15 above in which other variables were kept constant. This, of course, was to be expected on the basis of the chemical composition of these two tall oil fatty acid fractions.

Variation of the temperature of the reaction mixture during the hydrogenation of Acintol FA 2.--In experiments at room temperature in which Acintol FA 2 was hydrogenated in glacial acetic acid using 0.16 g. of Adams' catalyst and six grams of acceptor per 100 ml. of solution, it was found that the heat of the hydrogenation reaction was great enough to increase the temperature of the reaction mixture about eight degrees, Usually, the hydrogenation of the acceptor was complete before the apparatus was finally stopped, disassembled, and the final temperature measured. The value for the final temperature could be more accurately evaluated if the time that elapsed between the end of the reaction and the instant at which the final temperature was measured was accurately known, and if the effect of the natural cooling process upon the temperature at the end of the reaction was known.

The time difference mentioned above could be easily measured by recording the time at which the reaction was begun and the time at which the final temperature was measured. The time at which the reaction was completed could be ascertained from the plot of log P_o/P_t against time.

The effect of the natural cooling upon the temperature of the

reaction mixture, due to the lower temperature of the surroundings, could be evaluated by obtaining cooling data on a hydrogenation container filled with a solution typical of those used in the hydrogenation experiments. This data could be used to determine the cooling constant of Newton's law of cooling, and this be used to calculate the reaction mixture temperature at the end of the reaction.

Table 5 lists several runs in which the temperature at the beginning of the hydrogenation, the temperature at a recorded time after the

Table 5. Hydrogenation of Six Grams Acintol FA 2 in 100 ml. of Glacial Acetic Acid with 0.16 g. Adams' Platinum Oxide Catalyst

Run Number	T_{rm} °K	T_o °K	T_f^* °K	$(T_f^* - T_o)$ °C
25	298.2	291.3	303.4	+12.1
26	298.0	291.8	302.6	+10.8
27	298.2	292.9	304.4	+11.2
28	297.8	298.5	307.3	+ 8.8
29	298.0	298.5	306.5	+ 7.8
30	296.5	298.6	306.2	+ 7.6
31	298.5	305.5	310.7	+ 5.2
32	298.2	309.6	311.4	+ 1.8
33	298.2	313.2	313.1	- 0.1
34	298.2	318.2	317.5	- 0.7
35	298.2	319.2	316.8	- 2.0

*T_f is the corrected final temperature of the reaction mixture.

reaction was complete, and the room temperature were all measured. Also listed in the table is the adjusted final temperature for each run and the amount of change in the temperature of the reaction from t = 0 to t = time of completion of the reaction.

The much greater increase in temperature of the reaction mixture for experiments in which the initial temperature was considerably below

room temperature is quite reasonable, since at low starting temperatures there are two factors which contribute to the higher temperature of the solution at the end of the hydrogenation. These are the heating of the solution by the heat of the reaction and the heating of the system by the higher temperature of the surroundings. At starting temperature higher than room temperature, the natural transfer of heat from the reaction mixture to the surroundings and the rise in temperature of the system due to the heat of the reaction would be operating in opposite directions, so that the final temperature would not be as far removed from the initial temperature as was the case in the previously considered example.

Figure 3, page 25, consists of a graphic illustration of the values in Table 5 for $T_f - T_0$ plotted as ordinates and the initial temperature plotted as abscissas. The data were such that a reasonably satisfactory straight line for the points on the graph was drawn. This is only an approximation of the thermal effects of these hydrogenation reactions. Theroretically, as the values of initial temperature are extended over a wider range, the resulting plot would not be a straight line. The values for $T_f - T_0$ at very low temperature would be much more exaggerated than would be encountered on the straight line.

Considering the thermal effects of the reaction as above, the question arises as to exactly what temperature can be said to be that of a particular run; or more appropriately, what is the average temperature of one of these hydrogenation experiments? Of course the temperature is variable, as has been indicated, but it is desirable to compare the rate constants of different runs with those of other runs. Certainly, the

initial temperature cannot be reported with the rate constant representing any real relationship. On the other hand, neither the final nor the corrected final temperature is a very good quantity with which to report the rate constant. Some intermediate temperature would be more fitting for this purpose. In view of the nature of the experiments, the quantities measured, and especially considering the rapidity of the reactions which were studied, the mean temperature has been chosen as the value with which to report the rate constants. A constant temperature bath could have been used in these experiments, but since the reaction was so fast and the reaction bottles had such thick walls it is not likely that heat transfer would occur rapidly enough to produce very large gain in accuracy.

Determination of the energy of activation of the hydrogenation of Acintol FA 2.--In spite of the change in the temperature of the reaction medium during the hydrogenation, the determination of the rate constants was not as affected as might have been expected. The plots of the data obtained from the experiments yielded a very good straight line (see Figure 4). The value of the rate constants were found to increase as the mean temperature of the run was increased. It was possible, therefore, to utilize the Arrhenius law to obtain values for the apparent energy of activation of the reactions involved.

The dependence of the rate constant upon the mean temperature of the reaction mixture is illustrated in Table 6. The data listed therein were used to calculate a value of 3.51 kcal./mole for the hydrogenation of Acintol FA 2.

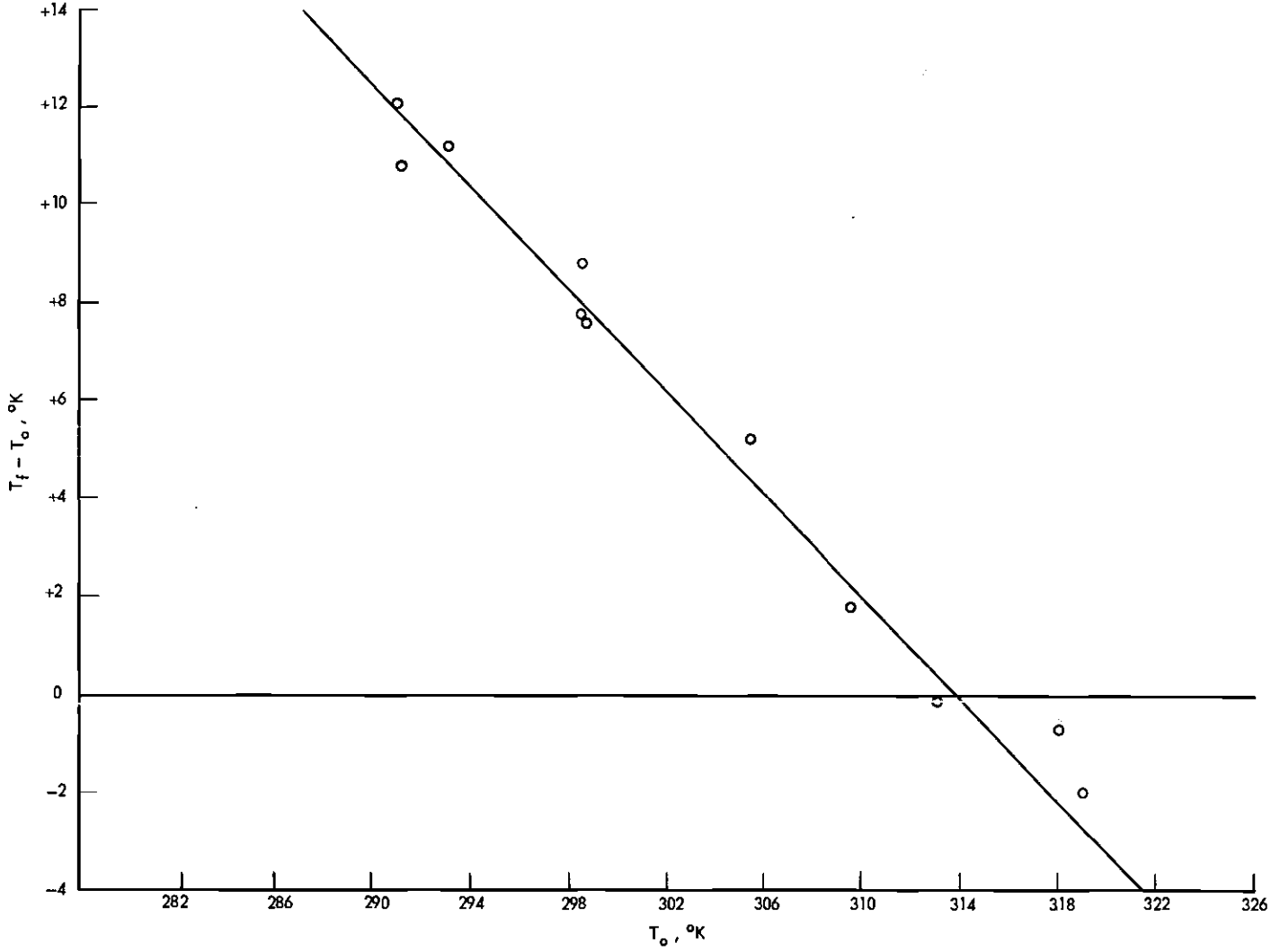

Figure 3. Temperature Change in the Hydrogenation of Acintol FA 2 Against Initial Temperature.

Table 6. Hydrogenation of 6.00 g. Acintol FA 2 in 100 ml. of Glacial Acetic Acid with 0.160 g. of Adams' Platinum Oxide Catalyst Lot C

Run Number	Mean Temperature ^{o}K	x 10^{4} $min.^{-1}/g.$	k x 10^{4} $min.^{-1}/g.$*
25	297.4	1450	1475
30	302.4	1573	1450
28	302.9	1648	1504
31	308.1	1790	1482
32	310.5	1887	1522
33	313.2	1952	1472
34	318.6	2138	1466

*Rate constant is given at 25°C; mean value 1481 ± 15.

Hydrogenation of Acintol FA 2 in cyclohexane and in tetrahydrofuran.--The hydrogenation of Acintol FA 2 was carried out in cyclohexane and in tetrahydrofuran as solvents. As was expected, the rate constants for these runs were considerably lower than for runs in glacial acetic acid as solvent. Table 7 lists these experiments for comparison with the typical runs in glacial acetic acid, as presented in the preceding table. As can be seen from these tables, the runs in the less acidic solvents gave rate constant values which were only 55 to 60 per cent as great as those in acetic acid.

When tetrahydrofuran or cyclohexane was used as solvent in the hydrogenation of Acintol FA 2, poisoning effects became more noticeable. The rate constant plot for these runs yielded a straight line initially, and this was the portion of the curves taken as correct. As the reaction proceeded, however, the curve deviated from a straight line and be-

gan to attain a less positive slope. This was found to begin at about two minutes and at about half the total hydrogen consumption and to continue to about five minutes where the uptake of hydrogen was essentially complete.

Table 7. Hydrogenation of Acintol FA 2 in 100 ml. Solution with 0.160 g. Adams' Platinum Oxide Catalyst

Run Number	Solvent	Mean Temperature °K	Rate Constant * x 10^4 $min.^{-1}/g.$
36	Tetrahydrofuran	295.9	820
37	Tetrahydrofuran	295.9	833
38	Cyclohexane	295.0	878
39	Cyclohexane	295.3	814

*Rate constants are corrected to catalyst lot C and to 25°C.

The product of the hydrogenation of Acintol FA 2.--The hydrogenation solution of a typical run was used for the isolation of the product of the reaction. The isolation was effected in a manner analogous to that used for the recovery of the product of the hydrogenation of Acintol FA 1. The solid crystalline material so obtained was recrystallized from alcohol and dried. Determination of its melting point gave a value of 69.2-69.8°C. The product as indicated by its melting point and as would have been expected from the composition of Acintol FA 2 was stearic acid. This is further evidenced by isolation of the product from another run, its esterification with methanol, and subsequent comparison of its gas-liquid-partition chromatogram with that of an authentic sample of methyl stearate.

Hydrogenation of esterified Acintol FA 2.--A sample of Acintol FA 2 was subjected to esterification conditions with methanol. The product of this reaction was isolated and hydrogenated. A quantity of 6.34 g. of the esters was dissolved in about 94 ml. of glacial acetic acid. The solution was found to hydrogenate with 0.16 g. of PtO_2 catalyst to give a rate constant corrected to 25°C of 1075 x 10^{-4} min./g. The rate constant was corrected on the assumption that the apparent energy of activation for these esters was comparable to that of methyl oleate.[1]

Hydrogenation of distilled tall oil (Acintol D).--Table 1 indicates Acintol D is only 69 per cent fatty acids. The chemical composition of Acintol D is somewhat higher in oleic acid content than are Acintol FA 1 and Acintol FA 2. The percentages of linoleic acid ($\Delta^{9,11}$) and linoleic acid ($\Delta^{9,12}$) in Acintol D are 9 per cent and 37 per cent, respectively, and it contains only 3 per cent saturated fatty acids.

Only a few runs were made using Acintol D as the hydrogen acceptor since its hydrogenation was so similar to Acintol FA 2. Table 8 lists the data for these runs.

Table 8. Hydrogenation of 6.00 g. Acintol D in 100 ml. of Glacial Acetic Acid with 0.10 g. Adams' Platinum Oxide Catalyst

Run Number	Mean Temperature, °K	Rate Constant * x 10^{4} min.$^{-1}$/g.
1	305.4	2564
2	305.7	2340
3	304.4	1922

*Rate constants are corrected to 25°C and catalyst lot C.

[1]See below, page 36.

Although the rate constants were not very reproducible, the runs indicated in Table 8 have an average rate constant of 0.2275. This is in fairly good agreement with the average rate constant value of 0.2110 for the 0.10 g. PtO_2 runs in the hydrogenation of Acintol FA 2.

The tabular description of the hydrogenation of all of the Acintols considered thus far indicates the very ready nature of these materials to accept hydrogen in glacial acetic acid using Adams' platinum catalyst. The experiments which were carried out using non-polar solvents on Acintol FA 2 yielded much lower rate constants, as was to be expected, since generally Adams' catalyst shows a marked increase in activity in acidic solvents. The rapid absorption of hydrogen by these tall oil fractions is contrasted by the results obtained on the attempted hydrogenation of another tall oil fraction, Acintol P, or tall oil pitch.

Attempted hydrogenation of Acintol P.--It was not possible to hydrogenate Acintol P in glacial acetic acid due to its low solubility in this solvent. Table 9 summarizes the qualitative solubility characteristics of Acintol P. The relatively low solubility of Acintol P in

Table 9. Solubility Characteristics of Acintol P

Solvent	Characteristic Solubility
Water	Insoluble
Methanol	Very slightly soluble
Ethanol	Very slightly soluble
Acetone	Soluble
Diethyl ether	Soluble
Acetic acid	Slightly soluble
Benzene	Very soluble
Cyclohexane	Slightly soluble
Tetrahydrofuran	Very soluble

most of the solvents tends to make the study of its hydrogenation rather difficult. As indicated in the table, the two solvents in which Acintol P was fairly soluble, benzene and tetrahydrofuran, were investigated as possible hydrogenation solvents. In experiments in which 6.0 g. of Acintol P was treated in the usual manner with hydrogen in the presence of 0.10 g. of PtO_2 in 50 ml. of tetrahydrofuran, there was no observable uptake of hydrogen. Almost identical results were obtained in the attempted use of benzene as solvent. The failure of Acintol P to accept hydrogen was also noted when either glacial acetic acid or small amounts of sulfuric acid was added to the tetrahydrofuran solution of the tall oil fraction.

Acintol P was investigated as possibly containing trace amounts of inorganic compounds which might be responsible for poisoning the hydrogenation catalyst. A sample of the material was extracted overnight with water and the resulting aqueous layer was tested with dilute solutions of barium chloride, silver nitrate, lead chloride, and with lead chloride test paper without obtaining a single positive test. The solution was also tested with 5 per cent $KMnO_4$ (aqueous) to yield a positive test. This indicates, of course, that some material which did not add bromine, and, consequently, probably wouldn't add hydrogen was extracted by the water, and that Acintol P contained some easily oxidizable material.

In another effort to ascertain if the tall oil pitch contained compounds which could be responsible for contamination the catalyst surface and therefore prevent reduction of the acceptor, samples of the material in benzene solution were shaken with large quantities of Raney nickel catalyst for extended periods of time. This should have resulted in the adsorption of the usual catalyst poisons which could have been present. After removal of the nickel, the Acintol P was again treated

with hydrogen in benzene solution in the presence of 0.10 g. of PtO_2. Again, the hydrogenation failed. It was discovered, however, that if such an attempted hydrogenation was permitted to continue overnight, the pitch would absorb some hydrogen. The quantity of hydrogen was equivalent to about 0.014 moles. If one assumes an average molecular weight of 300 for the compounds which constitute Acintol P, then 6.0 g. of this material would contain 0.02 moles of the compounds. Further, if each compound is assumed to contain one double bond, then there should have been an uptake of hydrogen which corresponds to this number of moles. The initial failure to achieve this in these experiments and then the approach to this value after treatment with Raney nickel indicates that either there is enough catalyst poisons in Acintol P to render it impractical to hydrogenate, or that the catalyst is being rendered ineffective in some other manner. This last statement is based upon the observation that in almost every case of the attempted hydrogenation of Acintol P, the catalyst was contained in the hydrogenation bottle as a gummy mass which tended to adhere to itself. Thus, it is concluded that the ineffectiveness of the catalyst was likely due to the mechanical trapping of the catalyst or strong adsorption of some component of the tall oil pitch. This was further indicated in the fact that after some of the acidic materials in tall oil pitch had been extracted and then subjected to hydrogenation conditions as usual, they were hydrogenated to some extent over a reasonable time span of about one half to one hour. It should be noted, however, that these acidic materials were extracted into acetic acid solution, and that the resulting solution was hydrogenated as such. The most favorable condition found was that of the

hydrogenation in the usual manner of 100 ml. of glacial acetic acid extract of Acintol P with 0.10 g. of Adams' catalyst. This particular run yielded an uptake of hydrogen equivalent to 0.01 moles in only 28 minutes. This did not permit the obtainment of a rate constant, however.

Hydrogenation of Tall Oil Rosin

Tall oil rosin was supplied by West Virginia Pulp and Paper Co. Complete specifications were not available, but it is known that the material consists principally of various resin acid isomers. The maximum amount of fatty acids present was 5 per cent. Larger amounts of catalyst were utilized in the hydrogenation of this tall oil fraction than in the Acintol fatty acid fractions. Both alcohol and acetic acid were investigated as solvents for the reaction, and the rate constants given in Table 10, page 33, are for the initial rate of hydrogenation. Due to the presence of poisons or perhaps due to the fact that the material consisted of a mixture of several isomeric resin acids, the plots were not as satisfactory as desired for these runs. Isomeric resin acids would show considerable variation in their hydrogenation rates, since the fused ring system of the phenanthrene type structure can give rise to large steric differences in these compounds. The different possible positions for double bonds in this ring system together with the effects of cis and trans ring fusion would be responsible for these steric differences.

As the data for runs 1, 2, 3, and 4 in Table 10 indicate, the amount of acceptor available in the hydrogenation solution does not appear to have a significant effect upon the rate constant, at least in the range of concentrations studied. In this range, there certainly should have been enough acceptor available to keep the catalyst surface saturated

Table 10. Hydrogenation of Tall Oil Rosin in 100 ml. Solution with 0.40 g. Adams' Platinum Oxide Catalyst Lot A

Run Number	Solvent	Acceptor Wt. g.	Temperature °K	k x 10^4 min.$^{-1}$/g.**
1	HOAc	12.00	301.6	459
2	HOAc	12.00	302.8	411
3	HOAc	6.00	303.2	411
4	HOAc	6.00	306.5	453
5	HOAc	6.00	298.5	643
6	HOAc	6.00	303.0	519
7	95% EtOH	6.00	300.2	242
8	95% EtOH*	6.00	300.6	542
9	95% EtOH*	6.00	303.2	509
10	95% EtOH*	6.00	303.4	506

*Runs 8-10 contained sulfuric acid at a concentration of 0.02-0.03 M.

**Rate constants are corrected to 25°C and catalyst lot B.

or covered to its capacity. The experiments in acetic acid solvent, identified as runs 5 and 6, appear to be entirely too large relative to the first four runs listed. This is due to the manner in which they were conducted. Run 5 was conducted after the acceptor had been allowed to stand in the acetic acid solution for three days. The catalyst was added to the solution and hydrogenation then carried out. Run 6 was exactly the same as run 5 except that the solution was heated to 110°C, allowed to cool to 60°, reheated to 110°, and allowed to cool to room temperature. After addition of the catalyst, hydrogenation was carried out in the usual manner. These two runs gave results which appear to be further away from the average value of the rate constant for runs 1-4 (434×10^{-4} min.$^{-1}$/g.) than could be caused by experimental error. The higher rate constants obtained for these runs are undoubtedly due to some change in

the acceptor, perhaps caused by the action of the acetic acid. This change could cause the rate constant to be increased if the new substance produced, hydrogenated more readily. Isomerization of the acceptor molecules could be caused by both heat and acid action, but both of the actions might lead to the formation of different isomeric mixtures, which may have significantly different rates of hydrogenation.

All the hydrogenations which were conducted in 95 per cent ethanol were not carried out in the same manner. Run 7 was executed in a manner exactly analogous to runs 1-4 and to most of the runs reported in this thesis. Runs 8-10, however, all contained small amounts of added sulfuric acid. Runs 8 and 9 were approximately 0.014 M in sulfuric acid. Number 10 was approximately 0.028 M in sulfuric acid. It should be noted that runs 9 and 10 were carried out at very nearly the same temperatures. In spite of the fact that the values listed in the table are corrected to 25°C, these corrections may not represent the base values for the listed rate constants. In the first place, the energy of activation used in the corrections was that obtained for the hydrogenation of abietic acid, or more exactly, for diamylammonium abietate in glacial acetic acid solution. Since in different solvents the activity of the catalyst varies, there is no certainty that the activation energy will be the same as the nature of the hydrogenation medium is varied. This would appear to be especially true if added mineral acid were present, as in the case of runs 9 and 10.

The product of the hydrogenation in acetic acid solution was isolated by precipitating the water insoluble materials by the addition of water. After five recrystallizations, the product had a melting point

of 162-165°C. The product, although recrystallized several times, was no doubt a mixture of isomeric resin acids. No attempt was made to isolate individual components of this mixture.

Hydrogenation of Tall Oil Constituents or Their Derivatives

It was considered of interest to investigate the hydrogenation of some of the principal constituents of tall oil in a purer form than was encountered in the various tall oil fractions used in the above experiments. The principal fatty acid in tall oil is oleic acid as indicated above,[1] while the major resin acid is most likely abietic acid.[2] Because of this, these two acidic compounds were chosen as the most suitable representative materials for the study.

Hydrogenation of Oleic Acid

Oleic acid was hydrogenated in glacial acetic acid and in cyclohexane. The data are listed in Table 11. The rate constants for runs 1 and 2 are not greatly different from those obtained for the hydrogenation of Acintol FA 1 and Acintol FA 2 using the same amounts of catalyst. It is also seen by the values given for runs 3 and 4 that they are at least of the same order of magnitude as those obtained for the hydrogenation of Acintol FA 2.

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[1] See above, page 7.

[2] Though not a primary resin acid itself, abietic acid is formed by isomerization of these primary acids through treatment with either heat or acid (14). During the course of their origin, tall oil resin acids are subjected to both heat and acid treatment.

(14) J. Simonsen and D. Barton, The Terpenes, Vol. III, Cambridge at the University Press, New York, N.Y., 1952, pp. 379-381.

Table 11. Hydrogenation of 6.00 g. Oleic Acid in 100 ml. Solution with 0.10 g. of Adams' Platinum Oxide Catalyst Lot A

Run Number	Solvent	Mean Temperature ^{o}K	$k \times 10^{4} min.^{-1}/g.$*
1	Acetic Acid	303.2	1985
2	Acetic Acid	302.6	1911
3	Cyclohexane	304.2	501
4	Cyclohexane	303.9	333

*Rate constants are correxted to 25°C and catalyst lot C.

Hydrogenation of Methyl Oleate

The greater ease of purification of the methyl ester of oleic acid and its more facile use in liquid-vapor-partition chromatography identification of the product, along with the fact that the rate of hydrogenation was not expected to be greatly different from that of the parent acid made this material seem appropriate for use in the determination of the activation energy for the hydrogenation of the double bond in the oleic acid molecule. Table 12 lists the data obtained in several experiments in the hydrogenation of methyl oleate. The above data yielded a value of 4.52 kcal./mole for the energy of activation of the hydrogenation of methyl oleate.

The product of the hydrogenation of methyl oleate was isolated in some of the runs listed below. After drying, the solid material obtained had a melting point of 39.4-40.4°C. Through comparison of gas chromatograms, it was determined that the product was methyl stearate.

Hydrogenation of Abietic Acid

Abietic acid was isolated from tall oil rosin for use in most of the runs conducted for this material. The data are summarized in Table

Table 12. Hydrogenation of 6.35 g. Methyl Oleate in 100 ml. of Glacial Acetic Acid with 0.10 g. Adams' Platinum Oxide Catalyst Lot C

Run Number	Mean Temperature °K	k x 10^4 min.$^{-1}$/g.*
1	293.1	1166
2	293.2	1114
3	294.5	1069
4	299.7	1234
5	305.8	1122
6	311.5	1044
7	319.5	1177

* Rate constants are corrected to 25°C; mean value 1132 ± 41.

13. The hydrogenation rate constant of abietic acid was only 0.0350 min.$^{-1}$/g. This is lower than the rate constants obtained for the hydrogenation of oleic acid or Acintol FA 2 by a factor of five or six. Data for the hydrogenation of these fatty acid compounds are not available for 0.40 g. PtO_2 which was used for the experiments on abietic acid.

Aside from the slower nature of the reaction in the case of abietic acid, another pecularity was noted.[1] When the plots of the values for log P_0/P_t against time were made, it was found that the graphs obtained were fitted easily to a straight line at the beginning of the curve, but it then began to deviate from a straight line as the time

Table 13. Hydrogenation of 6.00 g. Abietic Acid in 100 ml. of Glacial Acetic Acid with Adams' Platinum Oxide Catalyst Lot A

Run Number	Catalyst Wt. g.	Mean Temperature °K	k x 10^4 min.$^{-1}$/g.*
1	0.40	296.8	343
2	0.40	304.9	351
3	0.40	296.8	348
4	0.40	311.2	302
5	0.80	297.2	290

*Rate constants are corrected to 25°C and catalyst lot B.

[1]See Figure 4, page 44.

elapsed, and finally began to yield a second straight line. This line had a significantly smaller slope than that part of the curve used to obtain the values presented in Table 13. These smaller slopes yielded rate constants on the order of 5-10 x 10^{-4} min.$^{-1}$/g. This may be explained on the basis of a two step process; i.e., the partial hydrogenation of the abietic acid to an intermediate which occurs at a more rapid rate and the subsequent hydrogenation of the intermediate at a very much slower rate. This same effect was noted in the hydrogenation of diamylammonium abietate. Since a greater volume of data are available for diamylammonium abietate, the consideration of this phenomenon will be dealt with in the following discussion.[1]

Hydrogenation of Diamylammonium Abietate

Since it was found that diamylammonium abietate was purified more easily than abietic acid, and since the salt would be converted into the free acid under the conditions (in glacial acetic acid solution) of the hydrogenation experiments, it was used in a hydrogenation study. The presence of diamylammonium acetate in the hydrogenation solution may have altered the activity of the catalyst, but it would not be expected to have had a very large effect.[2] Furthermore, an effect produced by this material would be expected to be constant through the study.

Study of the initial reaction rate constants for hydrogenation in glacial acetic acid.--In order to observe the dependence of the reaction rate

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[1] See below, page 42 .

[2] Catalytic hydrogenation has been used extensively to prepare amines, and it follows that the catalyst surface is not rendered ineffective by the presence of these materials.

constant upon the weight of catalyst, a hydrogenation study was carried out on diamylammonium abietate in glacial acetic acid using varying amounts of Adams' platinum oxide catalyst. The data obtained from this investigation are listed in Table 14.

Table 14. Hydrogenation of 9.14 g. Diamylammonium Abietate in 100 ml. of Glacial Acetic Acid Using Adams' Platinum Oxide Catalyst

Run Number	Catalyst Lot	Catalyst Wt. g.	Temperature °K	$k \times 10^4 min.^{-1}/g.$*
1	B	0.20	301.2	385
2	B	0.30	301.2	394
3	B	0.40	298.2	351
4	A	0.40	300.4	300
5	A	0.40	300.4	300
6	A	0.40	300.5	297
7	A	0.40	301.2	280
8	A	0.40	299.4	274
9	A	0.40	301.7	270
10	B	0.50	301.2	286
11	A	0.60	297.5	262
12	B	0.60	301.2	260
13	B	0.60	301.2	258

*Rate constants are corrected to 25°C and catalyst lot B.

The fairly good reproducibility in the 0.40 g. runs should be noted. These experiments, runs 3-9, have an average value of 296 x $10^{-4} min.^{-1}/g.$ with an average deviation of 6.2 per cent. This applies to all these runs. When the values for the rate constants of runs 4, 5, and 6 are examined, it is seen that these runs have an average deviation of only 0.33 per cent. It will also be noted that for the catalyst weight range of 0.40 - 0.60 g., the reaction rate is directly proportional to the weight of catalyst.

A study was also conducted in which the quantity of acceptor was

varied, and the influence of this on the rate constant was observed. This is summarized by the data in Table 15.

Table 15. Hydrogenation of Diamylammonium Abietate in 100 ml. of Glacial Acetic Acid with 0.40 g. of Adams' Platinum Oxide Catalyst

Run Number	Catalyst Lot	Acceptor Wt. g.	Temperature °K	Rate Constant* x 10^4 $min.^{-1}/g.$
14	B	5.14	302.2	291
15	C	5.37	298.5	337
16	C	5.53	298.4	337
17	A	6.00	296.5	341
18	C	7.06	298.2	332
19	B	7.14	301.2	323
20	B	7.14	302.2	318
21	C	7.79	298.2	345
22	C	8.71	298.2	333
23	C	9.14	298.2	317
6	A	9.14	300.5	297
9	A	9.14	301.7	270
24	C	9.52	298.2	330
25	C	10.44	298.2	340
26	B	11.14	303.2	284
27	C	11.52	298.2	328

*Rate constants are corrected to 25°C and catalyst lot B; mean value 320 $\pm$ 15.

This table indicates that the weight of acceptor used in the hydrogenations has little if any effect upon the rate constants. Thus, the rate of hydrogenation is independent of the concentration of acceptor.

The weight of 9.14 g. of diamylammonium abietate was used for all of the other studies involved in this work since it is equivalent to 6.00 g. of the free acid on a molar basis. This is the quantity of abietic acid which was used in the study of its hydrogenation.

The apparent activation energy for the hydrogenation of this material was determined by examining the effect of varying the temperature

at which the hydrogenation was carried out. The data for this determination are presented in Table 16.

Table 16. Hydrogenation of 9.14 g. Diamylammonium Abietate in 100 ml. of Glacial Acetic Acid with 0.40 g. of Adams' Platinum Oxide Catalyst

Run Number	Catalyst Lot	Temperature ^{o}K	Rate Constant x 10^{4} $min.^{-1}/g.$	Corrected * Rate Constant x 10^{4} $min.^{-1}/g.$
28	B	318.2	510	279
29	B	318.2	509	279
30	B	311.2	368	287
31	B	311.2	409	274
32	B	305.7	409	323
33	B	305.7	429	291
9	A	301.7	301	270
7	A	301.2	308	280
34	B	300.7	302	279
35	B	300.7	287	266
6	A	300.5	319	297
4	A	300.4	321	300
5	A	300.4	321	300
8	A	299.4	284	274
36	B	294.2	216	247
37	B	294.2	216	247
38	B	288.2	211	295
39	B	288.2	210	294
40	B	288.2	206	288

*Corrected to $25^{o}C$ and catalyst lot B; mean value 294 ± 14.

The data given in Table 16 were used to evaluate the apparent activation energy for the hydrogenation of diamylammonium abietate. The value found was 5.35 kcal/mole. This was also assumed to be the activation energy for the hydrogenation of abietic acid under similar conditions.

In addition to the studies described above, several experiments were carried out in an attempt to observe the change of the rate constant as the initial pressure of hydrogen was changed. The data which

have been collected are tabulated in Table 17.

At low initial absolute pressure it is seen that the rate constant value is somewhat higher than at the higher pressures, indicating that the reaction in this case is not quite first order with respect to hydrogen over an extended range of pressures. The table describes a pressure

Table 17. Hydrogenation of 9.14 g. Diamylammonium Abietate in 100 ml. of Glacial Acetic Acid Using 0.40 g. of Adams' Platinum Oxide Catalyst Lot B Temperature 301.2°K

Run Number	Initial Absolute Pressure p.s.i.	$k \times 10^4$ min.$^{-1}$/g.*
41	17.21	417
42	17.26	377
43	32.34	398
44	32.40	386
45	46.77	326
46	64.34	314
47	64.37	290

*Rate constants are corrected to 25°C.

range of approximately 50 p.s.i. In each individual run, however, a pressure drop of only three pounds per square inch was noted, and the data for each run were fitted easily to a straight line when log P_o/P_t was plotted against time. Such phenomena are not unusual.

Complete Hydrogenation in Acetic Acid.--The complete hydrogenation of both abietic acid and diamylammonium abietate were characterized by what appeared to be a two step process. This is indicated in Figure 4, page 44, by the plot of data obtained in a typical run.

Characteristics of the reaction.--For the experiments described above, there was always a very rapid uptake of hydrogen occurring during

the first two to three minutes of the run. This portion of the experiment yielded the rate constant data which are tabulated and discussed in the preceding pages.[1] After this first phase of the experiment, there followed a period of four to five more minutes in which the plot of the data did not fit a straight line but very decidedly was curved downward toward the time axis. This then was followed by a slow uptake of hydrogen which again appeared to obey first order kinetics as evidenced by the plot of log P_o/P_t against time. The rate constants obtained from this last phase of each of the reactions, while very difficult to reproduce, in most cases did fit a straight line for a very long period of time. In summary, a typical hydrogenation run at 27° yielded the data which could be stated as below:

The initial fast reaction gave a rate constant of 325×10^{-4} min.$^{-1}$/g. from zero to two minutes time.

The transition phase gave an approximate rate constant of 50×10^{-4} min.$^{-1}$/g. from two to seven minutes time.

The final slow reaction gave a rate constant of 10×10^{-4} min.$^{-1}$/g. from seven to 60 minutes time.

It was generally observed that the transition phase began in the vicinity of hydrogen uptake corresponding to 0.02 moles of hydrogen for a run using 0.02 moles of substrate. In spite of the difficult reproducibility of the rate of the third phase, it was usually found that the value was at least qualitatively related to that of the first phase rate constant. In general, when the first phase rate constant was high, that of the third phase was low, and the transition or second phase was

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[1] See Figure 4, page 44.

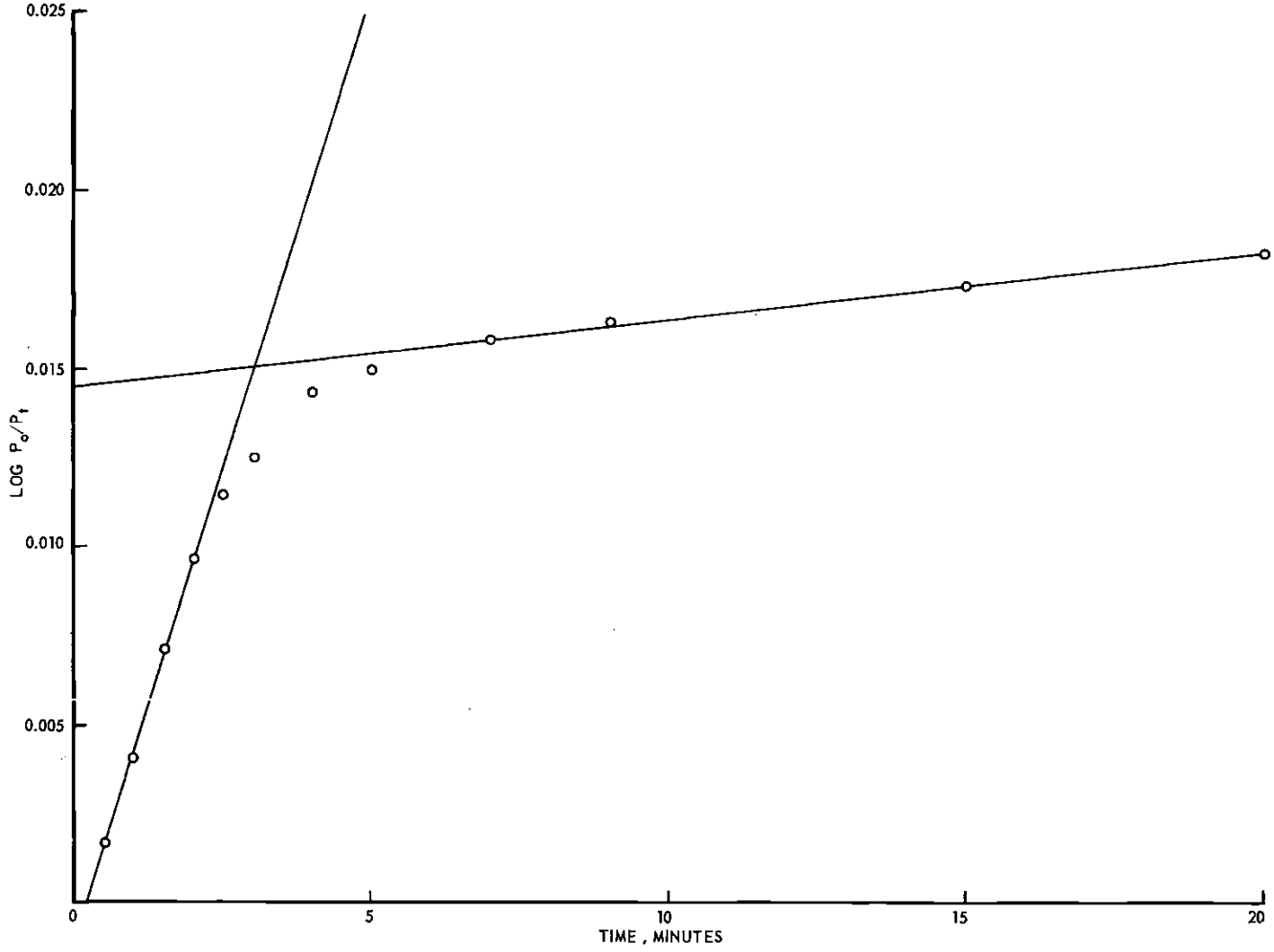

Figure 4. Typical Plot of Log P_o/P_t Against Time, in the Hydrogenation of Diamylammonium Abietate.

short. On the other hand, if the value for the first phase rate constant was low, then the transition phase was relatively long, and the third phase rate constant was high.

Several postulates could be offered to interpret these observations; namely:

1. The catalyst surface could have been poisoned during the reaction.

2. The acceptor could have been isomerized by the acetic acid solvent.

3. The acceptor could have been isomerized by the catalyst surface.

4. The reduction could have proceeded by a two or poly-step mechanism in which the reaction involved first the acceptor's being reduced to one or more dihydro-compounds and then these being reduced further at a slower rate to a tetrahydro-compound.

Non-poisoning of the catalyst.--Aside from the fact that the plot changed from a straight line to a curve and once again to another straight line indicating that postulate one above is not correct, it was very easily shown that this was not the case on the basis of other experiments. A hydrogenation of diamylammonium abietate was conducted in the usual manner, except the hydrogenation was discontinued after 1.11 moles of hydrogen per mole of acceptor had been absorbed. The catalyst was filtered off and then replaced by fresh PtO_2. The pressure of the system was adjusted to equal that measured when the reaction was interrupted. After the hydrogenation was resumed, the data were collected, and the customary plot was made. It was found that changing to fresh catalyst had no appreciable effect upon the rate of hydrogenation. The transition phase occurred as usual, and the third phase was typical of those cases which

were begun normally and continued to completion.

Non-isomerization of the substrate by the acetic acid solvent or platinum oxide.--A hydrogenation experiment was conducted in which first the acceptor was agitated in the presence of non-reduced Adams' catalyst and glacial acetic acid solvent for fifteen minutes in the absence of hydrogen. This was equivalent to the time at which the slow third phase of the reactions usually appeared. Hydrogen then was admitted to the system, and the reaction was started. This resulted in the normal kind of kinetic data.

The uncorrected initial rate constant obtained was 414×10^{-4} min.$^{-1}$/g.

The uncorrected final rate constant was 10.8×10^{-4}min.$^{-1}$/g. at a reaction temperature of 31.7°C.

These values are higher than the typical ones presented earlier, but the temperature of this reaction was significantly higher. The conclusion here is that acetic acid does not isomerize abietic acid within fifteen minutes to an extent which effects the rate constants of the hydrogenation of this compound.

Non-isomerization of the substrate on the catalyst surface.--It was found that if abietic acid was agitated overnight in dry chloroform solution and in the presence of pre-reduced Adams' catalyst, the solution yielded an infrared spectrum identical to a freshly prepared solution of abietic acid in chloroform.

Additional evidence against postulate three[1] was obtained in another experiment. Agitation of diamylammonium abietate with previously reduced PtO_2 followed by hydrogenation with fresh catalyst after the

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[1]See above, page 45.

former had been removed by filtration resulted in the following data:

Uncorrected initial rate constant 516 x 10^{-4} $min.^{-1}/g.$

Uncorrected final rate constant 12 x 10^{-4} $min.^{-1}/g.$

Reaction temperature 31.4°C.

These results indicate that abietic acid is not isomerized on the platinum surface within fifteen minutes in a way which would cause the rate constant of the hydrogenation of this compound to be reduced. Indeed, the data are of higher value than would have been expected. This may be due to the fact that the first quantity of Pt used removed some trace amounts of poisons from the solution.

Removal of poisons from the solution by previously reduced catalyst is further indicated by experiments similar to the one just described. When the substrate was agitated with pre-reduced catalyst in the absence of hydrogen and then hydrogenated using the same catalyst, the initial rate constant was found to be 85 to 110 x 10^{-4} $min.^{-1}/g.$ at 31°C for several different runs. This might also be explained on the basis that the substrate molecules may have been adsorbed upon the catalyst to produce a saturated surface. Such a situation could cause the hydrogenation to proceed more slowly, since the hydrogen would have fewer catalyst sites upon which to be adsorbed. It has been shown in other hydrogenations that pre-adsorption of the substrate on platinum, rhodium, and nickel catalyst can inhibit the reaction (15). While this explanation appears to have some validity from these data, it does not account for the higher rate constant value obtained after agitation of the acceptor with reduced PtO_2,

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(15) O. Beeck, Discussions Faraday Society, 8, 118 (1950), P. Emmett, Catalysis, Vol. III, Reinhold Publishing Corporation, New York, N.Y., 1955, p. 57.

removal of the Pt, and replacement with fresh PtO_2 for the subsequent hydrogenation.

These experiments jointly rule out three of the four postulations regarding the observation of the three phase hydrogenation data.

The kinetics of the reaction exist as were found, not because the catalyst surface is poisoned during the reaction, not because the acceptor is isomerized by the acetic acid solvent, and not because the acceptor is isomerized by the catalyst, but for some other reason. The other postulation was that the rate data result from competing first order reactions. It was further suggested that the abietic acid was undergoing partial hydrogenation to some dihydroabietic acid which is hydrogenated at a slower rate than the parent acid.

Competition of multiple first order reactions.--Support for this postulate was gained through another experiment in the hydrogenation of diamylammonium abietate. A quantity of 0.02 moles of this salt was hydrogenated until it absorbed 0.0186 moles of hydrogen. The product was then isolated, recrystallized once, dried, and found to have a melting point of 137-146°C. The ultraviolet spectrum of this material revealed λ_{max} at 241 mμ having an extinction coefficient of 6,210. This indicates there was 25.6 per cent abietic acid present, assuming that the hydrogenated constituents do not absorb light at this chosen wave length.

In order to evaluate this information, the several possible courses of the reaction need to be considered.

1. Abietic acid could be reduced directly to a tetrahydroabietic acid.

2. Abietic acid could be reduced first to a dihydroabietic acid

completely before any of the dihydroabietic was reduced to tetrahydroabietic acid.

3. Abietic acid could be reduced first to a dihydroabietic acid, and the product could be reduced further to tetrahydroabietic. The two reductions could be in competition after a significant amount of dihydroabietic acid had been produced.

If the first case was operative, at the absorption of 0.0186 moles of hydrogen per 0.02 moles of acceptor there should have been left slightly more than 50 per cent abietic acid. Also, if this had been the case, Figure 4 should have consisted of a single straight line ending at the consumption of 0.02 moles of hydrogen.

If the second case was operative, at the absorption of 0.0186 moles of hydrogen per 0.02 moles of acceptor there should have been only slightly more than 0 per cent abietic acid. In addition to this, the two straight lines in Figure 4 would be expected to intersect at a single point instead of curving into each other. This point should correspond to the consumption of exactly 0.02 moles of hydrogen.

If the third case was operative, at the absorption of 0.0186 moles of hydrogen per 0.02 moles of acceptor, most of the hydrogen would have been consumed by the abietic acid, but part of it would have been required for the further reduction of the dihydroabietic acid to tetrahydroabietic acid. This would be expected to result in the presence of more than 0 per cent and less than 50 per cent abietic acid when the reaction was stopped. Furthermore, this case would be expected to produce a curve like that shown in Figure 4.

In addition to this, it was usually noted that the transition

phase of the hydrogenation began at the pressure drop which corresponded to the uptake of approximately one mole of hydrogen per mole of acceptor. This leads strong support to case three.[1] Also the fact that the two rate constants in each run seem to be intererrelated would be in agreement with the suggestion that these constants are for the rates of two competing first order reactions in both phases of the reaction which obey first order kinetics.

This can be explained in the two following manners:

1. Abietic Acid + H_2 $\xrightarrow{k_1}$ Dihydroabietic Acid

2. Dihydroabietic Acid + H_2 $\xrightarrow{k_2}$ Tetrahydroabietic Acid

First if k_1 and k_2 were the rate constants for these reactions, and if k_1 were larger than k_2 by a factor of approximately 100 (as were the rate constants for the first and third phases in the actual hydrogenation of abietic acid in this work), they could be expected to exert an effect upon the apparent rate constants for their reactions in a manner analogous to that observed. At the beginning of the hydrogenation, k_1 would be solely responsible for the apparent value of the rate constant and for the rate of the reaction. As the reaction proceeded, however, and the concentration of dihydroabietic acid became significant, the second reaction would begin to occur, and the apparent rate of the reaction would be a function of both k_1 and k_2. The apparent rate would not change significantly, because k_2 would be so small relative to k_1 that its presence would not be noticed.

As the amount of abietic acid was decreased in the reaction mixture, the first reaction would start becoming less significant in its

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[1] See above, page 49.

contribution to the apparent rate of the reaction. At this time, the apparent rate constant would be a function of both k_1 and k_2, and both of these could be contributing to its value to a varying degree. This would mark the onset of the transition phase of the reaction and its gradual conversion into the third phase. In the third phase of the reaction, the apparent rate constant would be a function of both k_1 and k_2, but k_2 would be the principal contributor to its value.

The appraisal of the reaction process as presented above is in accord with the interrelationship of the rate constants for the first and third phases of the reduction. If the reaction conditions were such that in general they would be expected to yield a slow rate for hydrogenation reactions, then the first phase of the process would be affected to the greatest extent. Such a situation could be expected to give a longer transition phase during which the amount of abietic acid would be decreased to such a low value that its hydrogenation would not be important toward the overall rate of the reaction. This could also leave enough abietic acid in solution and in competition for the catalyst surface with the now much more numerous dihydroabietic acid molecules to cause the observed rate constant for the third phase of the hydrogenation to be slightly larger.

In the other extreme case, the reaction conditions would be such that they would favor fast hydrogenations and would result in a very rapid conversion of the abietic acid into the much more slowly hydrogenated dihydroabietic acid. Consequently, the first phase of the reaction would appear to be very fast. Since the contribution of the half hydrogenation of abietic acid to the rate of the overall reaction would be quite significant and then rapidly become insignificant, the rate constant for the

third phase would be expected to be very slow. More nearly, it would be principally due to the hydrogenation of dihydroabietic acid,[1] since in this case there should be very little if any abietic acid left in the reaction mixture.

The second manner of explaining the results obtained for these hydrogenation reactions would also be made on the basis of the equations given earlier.[2] If k_1 is much greater than k_2, and dihydroabietic acid is hydrogenated preferentially to abietic acid, then the curve in Figure 4 could have been produced. During the initial part of the reaction, the reaction of abietic acid would be expected to predominate, but as the concentration of dihydroabietic acid increased and was preferentially adsorbed, its slow reduction would produce the retarding effect found during the second or transition phase of these reactions. Finally, as the remaining abietic acid was reduced to dihydroabietic acid, the last straight line in the plot of the data would be obtained.

All of these arguments and data, while not completely conclusive, seem to indicate strongly that the reduction proceeds through partial hydrogenation of the acceptor, followed by hydrogenation of the product so formed to the final tetrahydroabietic acid.

Selectivity of catalysts in hydrogenation of olefins.--It is generally known that hydrogenation reactions may be selective in the hydrogenation of one double bond instead of another in the same molecule or in different kinds of molecules, even in conjugated dienes. For example, the partial hydrogenation of 2-methyl-1,3-butadiene on platinum catalyst

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[1] See above, page 50, step 2.

[2] See above, page 50.

leads to 1,2 addition, 3,4 addition, and 1,4 addition of hydrogen (16). Limonene, a compound having a partially saturated ring, has been partially hydrogenated in the isopropenyl group to produce principally 1-methyl-4-(1-methylethyl)-1-cyclohexene (17). Although, there are not many experimental data on the subject, it is generally assumed that catalytic hydrogenation involves cis-addition of hydrogen to olefins (18). It is also thought that in hydrogenation reactions the olefin is adsorbed to the catalyst surface on its flattest side, and the hydrogen is added on this side of the molecule (19). This refers to hydrogenation in acidic medium, however, since 4-cholestene is hydrogenated in neutral medium to coprostane and in acidic medium to cholestane. This is illustrated in Figure 5, page 55. When the double bond is in the 5,6-position in the steroid nucleus, the same behavior is observed. Thus, cholesterol is hydrogenated with Pt in acidic medium to produce cholestane-3β-ol. (20).

A double bond in the 7,8- or 8,9-position in the steroid nucleus, it is not hydrogenated and isomerizes to the 8,14-position on palladium or platinum catalyst, as is illustrated in Figure 6, page 56. The isomerization is faster in acetic acid medium (21). This isomerization is thought

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(16) Corson, op. cit., pp. 79-80.

(17) V. Ipatieff, Ber., 43, 3546 (1910), P. Emmett, Catalysis, Vol. III, Reinhold Publishing Corporation, New York, N. Y., 1955, p. 83.

(18) Corson, op. cit., p. 97.

(19) L. Fieser, and M. Fieser, Steroids, Reinhold Publishing Corporation, New York, N. Y., 1959, p. 271.

(20) Ibid., pp. 272 and 27.

(21) Ibid., pp. 273.

to be an allylic rearrangement. The hydrogen atom removed and the one returned to another carbon atom both act from the same side of the molecules mentioned above. The side on which this occurs is also the flattest side of the molecule. The steroids seem to be a good class of compounds with which to draw similarities to the resin acids, since the former materials seem to be very well characterized and understood. This does not appear to be the case for the dihydroabietic acids.[1]

On the basis of the facts presented above, if there is any similarity between the behavior of the steriods and the resin acids on hydrogenation, it is readily seen that it would be exceedingly difficult to predict what might be the result upon hydrogenation of abietic acid. If simplifying assumptions are made, however, it is possible to describe the likely outcome of the hydrogenation.

The first assumption is that in the acetic acid solvent, abietic acid does not undergo isomerization. This is based upon the fact that acid isomerization of primary resin acids yields abietic acid and upon the results of experiments described earlier.[2] The second assumption is that if a dihydroabietic acid is produced first, it does not isomerize under the influence of either the catalyst or the solvent. This is made without substantiating evidence. The third assumption is that in the hydrogenation, the molecule is adsorbed on its flattest side, and cis-addition of hydrogen occurs on this side of the molecule. This assumption is made on the basis that the hydrogenation of the resin acids should parallel that of the steriods in this respect, since both classes of

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[1] See above, page 10.

[2] See above, page 46.

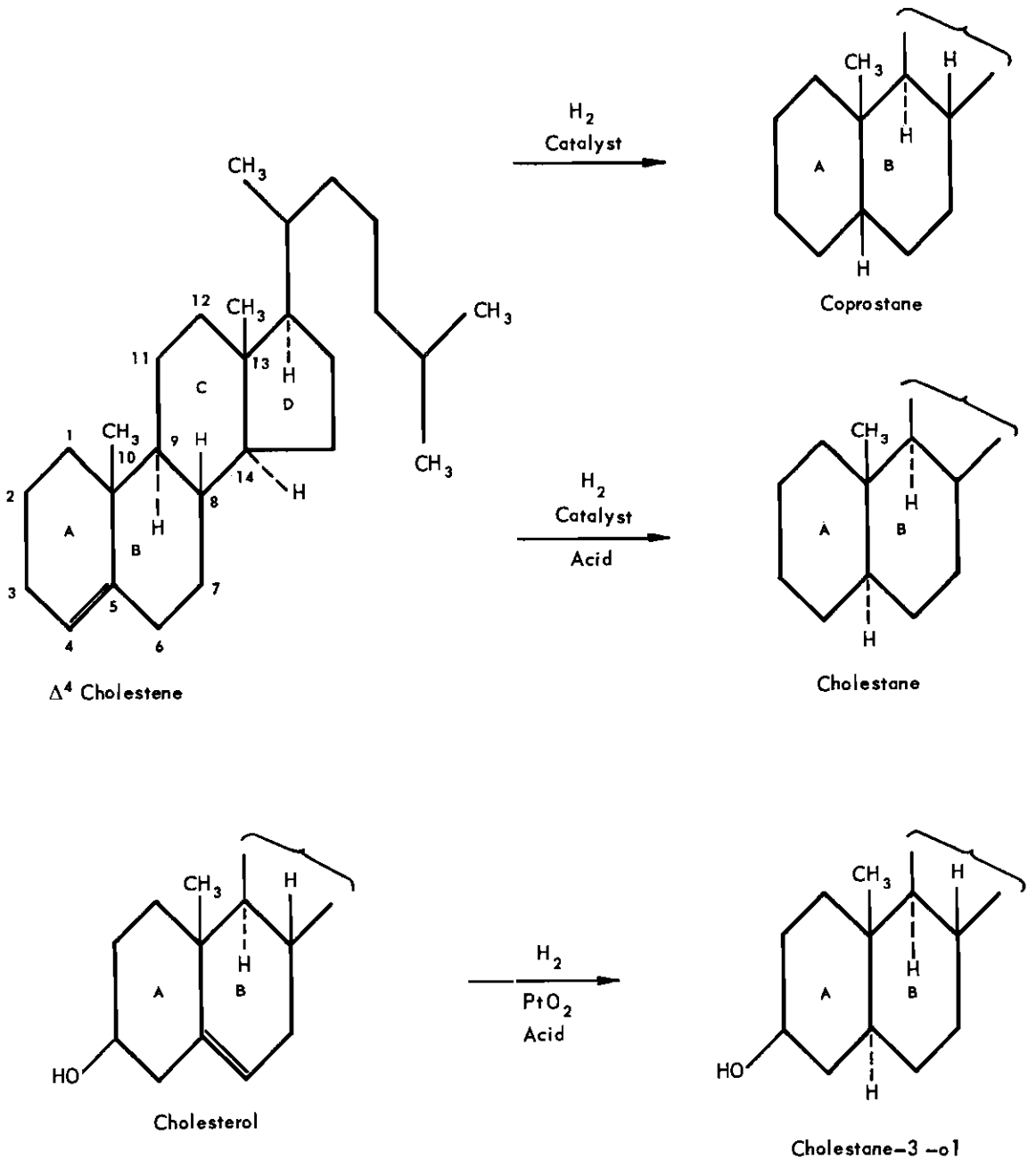

Figure 5. Some Steroid Hydrogenation Products.

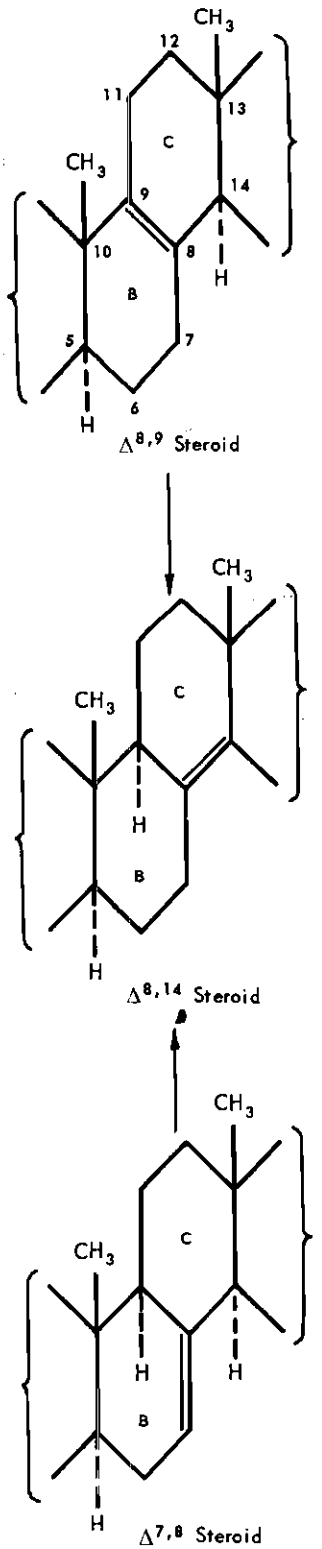

Figure 6. Isomerization of Unsaturated Steriods by Hydrogenation Catalysts.

compounds have ring structures related to saturated phenanthrene. With these assumptions, it is possible to say that the structure of the dihydroabietic acid produced is that which would result from addition of hydrogen to the abietic acid molecule in one of three possible manners. Addition to the 7,8-position would result in the formation of compound (I) in Figure 7, page 59, while addition to the 9,14-position would lead to compound (II). If the hydrogen were added in a 1,4-manner or to positions 7 and 9 in the abietic acid molecule, compound (III) would be produced.

The compound represented by structure (I) in Figure 7 has been prepared from abietic acid by reduction with lithium metal in liquid ammonia. It is fairly well characterized, but the sterochemistry of carbon 7 is not established (22). Preparation of a sample of this material using the procedure given by Kennedy (23), followed by its hydrogenation in the same manner that was most often used for abietic acid, yielded data which were plotted in a manner analogous to that used throughout this work. While the data were not as good as was desired, it was possible to approximate the rate constant value for the initial rate of hydrogenation to be 298×10^{-4} min.$^{-1}$/g. This value was obtained at a temperature of 28.4°C and is far too large to be identical with that usually obtained for the third phase of the hydrogenation of abietic acid. It is not greatly different from the rate constant obtained in the first phase of the hydrogenation of abietic acid. It should be pointed out that this dihydroabietic acid was not very soluble in glacial acetic acid. Normally 100 ml. of acetic acid was used in the hydrogenation runs. This

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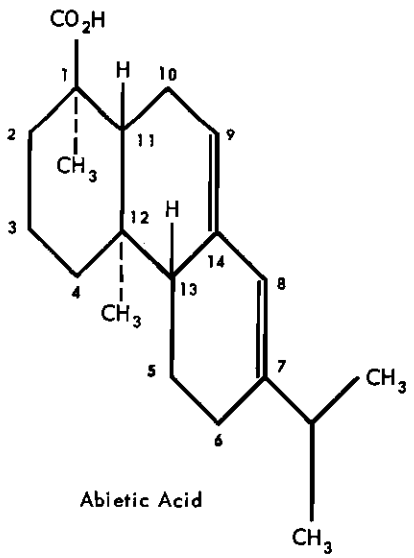
(22) Royals, op. cit., p. 151

(23) R. Kennedy, A Study of the Structure of a 7,8-Dihydroabietic Acid, Ph.D. Thesis, Emory University, 1956, p. 52.

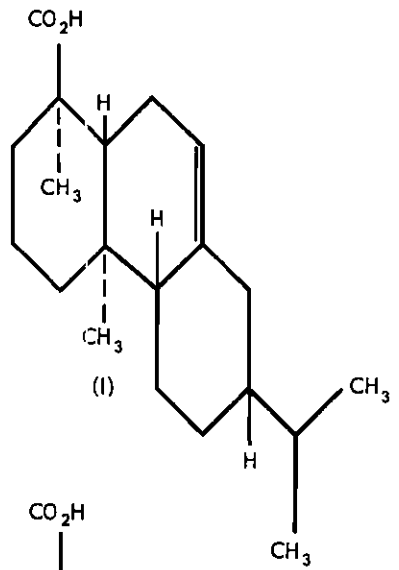
material required the use of 125 ml. of solvent to dissolve completely the quantity used in this reaction (0.02 moles). The product from the hydrogenation reaction was isolated and recrystallized from acetone and found to have a melting point of 177-178°C.

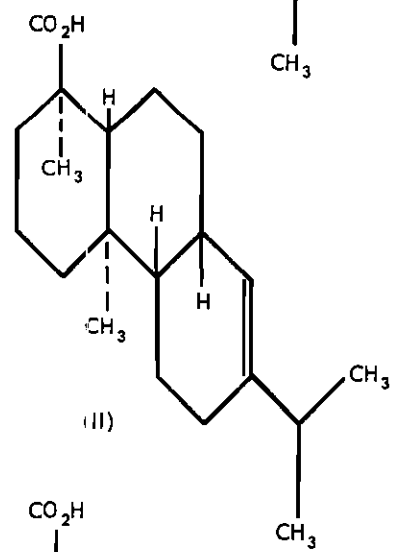
From this experiment it appears that an intermediate in the hydrogenation of abietic acid does not have structure (I) in Figure 7, but it will be recalled that the stereochemistry of carbon 7 in Royals' 7,8-dihydroabietic acid is not known. It would appear that the stereochemistry at this center could greatly effect the rate constants of hydrogenation of the possible diastereoisomers which could result from variation of the configuration at this carbon. The hydrogen which would be added at carbon 14 would be on either the same side or the opposite side of the molecule as the isopropyl group at carbon 7. If it were added on the same side of the molecule, this could lead to very strong 1,3-type interaction between these two groups. It may not be said from the data found that structure (I) is not the intermediate formed in the hydrogenation of abietic acid, but only that the intermediate formed is very likely not the same compound as that studied by Royals and Kennedy.

Since other dihydroabietic acids were not available through known syntheses, the only other reasonable approach to the problem seemed to be in the isolation of the dihydroabietic acid intermediate which is apparently formed in the hydrogenation of abietic acid under the conditions investigated in this work. It was also desired to attempt isolation of the products of total hydrogenation of abietic acid. In every attempt that was made, no success was achieved. It was not possible to separate the mixtures obtained at either half or total hydrogena-



Abietic Acid





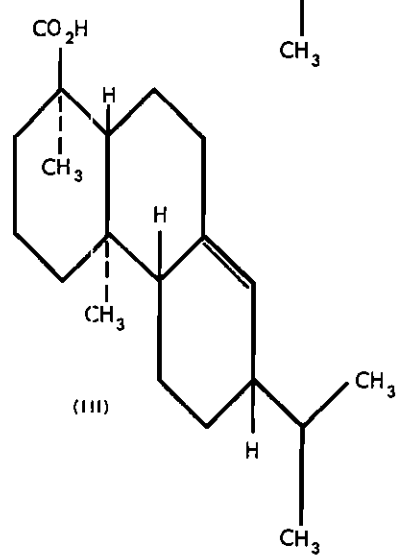


Figure 7. Possible Hydrogenation Products of Abietic Acid.

tion of the substrate.

While much work could have been conducted in an attempt to elucidate the structure of some of the products from these reaction, it was first imperative that pure compounds be obtained from the mixture of products. Various chromatographic techniques were utilized in an effort to achieve this but without success. Paper chromatography, elution chromatography, and gas-liquid-partition chromatography were all investigated as possibilities, but none of these were found to be suitable. Gas-liquid-partition chromatography appeared to be most promising, but the low volatility of the compounds investigated and the low thermal limit of the instrument available failed to produce satisfactory results.

CHAPTER III

EXPERIMENTAL

Introduction

All boiling points, melting points, and temperatures of reactions reported herein are uncorrected. Melting points were determined in capillary tubes in a circulating oil bath using a 360° immersion type thermometer.

Equipment and Instruments

The Hydrogenation Apparatus

The hydrogenation experiments reported herein were conducted in a Parr Pressure Reaction Apparatus, serial number 867, manufactured by the Parr Instrument Company, Incorporated, Moline, Illinois. Two different sizes of hydrogenation bottles were used with the apparatus. The total volume with the smaller bottles was 4.43 l. (24). There were three major parts of the apparatus. The first of these was a hydrogen storage tank of approximately four liter capacity which accounted for the major part of the total volume of the system. This tank was equipped with a laboratory test gauge of 60 p.s.i. capacity capable of being read to within 0.05 p.s.i. and with a thermometer well in which an ordinary 100° mercury thermometer was kept for measuring the temperature of the tank. By means of suitable valves, the tank was connected to the second part

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(24) J. Hecht, The Catalytic Hydrogenation of Quinolines, Unpublished M.S. Thesis, Georgia Institute of Technology, 1950, p. 28.

of the apparatus: a Pyrex glass reaction bottle of approximately 400 ml. capacity. The bottle, held on a mount connected to a motor through a shaker arm, was capable of oscillation. This last and third part of the apparatus, the motor, effected an agitation cycle of approximately 280 cycles per minute during the hydrogenation process. The hydrogenation bottle was connected through suitable valves to an oil type vacuum pump for evacuating the reaction bottle.

The Fractionation Column

Distillation of the solvents used in the hydrogenation experiments were conducted in a Todd Precision Distillation Assembly manufactured by the Todd Scientific Company, Springfield, Pa. The three foot fractionation column used had a diameter of 12 mm. and was packed with Podbelniak Heli-Pak random-type packing. The packing, made of tantalum, was 0.035 inch x 0.070 inch x 0.070 inch in size.

The Infrared Absorption Spectrometer

The infrared spectra mentioned herein were determined on a Perkin-Elmer Model 21 Infrared Double-beam Recording Spectrometer equipped with sodium chloride optics and cells. The spectra were determined in solution at approximately 5 per cent concentration and were usually recorded from 2.0 to 15.0 microns.

The Ultraviolet Absorption Spectrometer

The ultraviolet spectra of the abietic acid and diamylammonium abietate were made using a Beckmann DU spectrophotometer equipped with one centimeter quartz cells. The spectra were determined from an alcohol solution made by dissolving 0.0500 g. of the material in 95 per

cent ethanol and diluting to 50 ml.

The Polarimeter

A Lippich half-shadow polarimeter was used in conjunction with a sodium-vapor lamp as light source in the determination of the optical activity of diamylammonium abietate and other resin acid derivatives. The solutions to be tested were introduced into four decimeter glass tubes and placed in the instrument.

The Gas-Liquid-Partition Chromatography Instrument

The gas-liquid-partition chromatographic experiments were conducted in a Perkin-Elmer Vapor Fractometer Model 154 D. They were run on several different columns which are described later.[1]

Materials

Abietic Acid

Abietic acid was prepared from either Matheson, Coleman, and Bell technical grade abietic acid or from tall oil rosin by the method proposed in Organic Syntheses (25), with the exception that nitrogen gas was substituted for carbon dioxide gas which was recommended. The technical grade abietic acid was used in the beginning of this work but was abandoned later in favor of the tall oil rosin since this was found to give better yields of abietic acid. Since all of the batches of the acid were purified in the same manner, this indicates that the

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[1] See below, page 97.

(25) G. Harris and T. Sanderson, Organic Syntheses, Vol. 32, John Wiley and Sons, Incorporated, New York, N. Y., 1952, pp. 1-4.

tall oil rosin was richer in abietic acid, or resin acids which isomerize to abietic acid, than was the technical grade abietic acid. The material obtained in this work had a melting point of 163-165°C and showed an absorption maximum at 241 mμ with an extinction coefficient of 24,000. Optical rotation determination at 24.3°C in absolute ethanol yielded a specific rotation of -97° at the D line of sodium.[1]

Acetic Acid

Glacial acetic acid was purified by fractionation through the Todd column. The constant boiling fraction at 115.6° and 743 mm. pressure was collected and used as solvent in many of the hydrogenation experiments.

Acintols

Four tall oil fractions called Acintols were supplied by the Arizona Chemical Company, 30 Rockefeller Plaza, New York 20, N. Y. Specifications for these materials are given on page 13.

Acintol FA 1.--This material was used without alteration.

Acintol FA 2.--Acintol FA 2 was used as supplied.

Acintol D.--This material was also used without purification.

Acintol P.--Tall oil pitch or Acintol P was used as supplied in some hydrogenation experiments. In these experiments, however, it was not found possible to hydrogenate the material under the usual conditions used for the other Acintols, and catalyst poisons were suspected as responsible for this. In order to remove any possible poisons, the following treatments were carried out.

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[1]Reported optical rotation: -106° at 24.0° and at the D line of sodium.

A sample of 15 g. of Acintol P was agitated with 50 ml. of distilled water and allowed to stand overnight. Samples of the aqueous solution were tested with a 0.2 M solution of lead acetate (for possible presence of sulfide ion), with 0.1 M silver nitrate solution (for presence of halide ion), and with 0.1 M barium chloride (for presence of sulfate or sulfite ion). All of these tests gave negative results.

Approximately five grams of Acintol P was dissolved in 100 ml. of thiophene-free benzene and extracted with two portions of 25 ml. of distilled water. The aqueous extract was then washed with three 50 ml. portions of thiophene-free benzene followed by washing with a like number of 50 ml. portions of diethyl ether. Treatment of samples of the aqueous solution with the test materials, mentioned above, again resulted in all negative results. Other samples were treated with 5 per cent bromine in chloroform and 2 per cent potassium permanganate test solution. The bromine was not decolorized, but the potassium permanganate was reduced rapidly.

Six grams of Acintol P dissolved in 100 ml. of thiophene-free benzene was placed in a hydrogenation bottle with approximately one gram of moist Raney nickel catalyst. The mixture was agitated for 40 minutes on the hydrogenation apparatus but in the absence of air or hydrogen. Removal of the nickel by filtration and subsequent hydrogenation of the filtrate using 0.10 g. PtO_2 resulted in absorption of enough hydrogen to cause a decrease in pressure of only 0.25 p.s.i., or only approximately 10 per cent of the amount that would be expected on the basis of the iodine number of this material.[1]

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[1]See above, page 13.

In order to remove the acidic components of Acintol P for hydrogenation, 50 g. of this tall oil fraction in 120 ml. of thiophene-free benzene was extracted at reflux with 10.2 g. of 50 per cent sodium hydroxide solution for one hour. According to the saponification data for Acintol P,[1] this amount of base is a 10 per cent excess of that needed to saponify 50 g. of Acintol P. The benzene was removed under vacuum, and 250 ml. of water was added. After 15 minutes of continued refluxing, the mixture was cooled and extracted with four portions (50, 50, 50, and 100 ml.) of diethyl ether. The aqueous layer was acidified with sulfuric acid and then extracted with three portions (50, 50, and 100 ml.) of ether. These ether extractions were placed in a 500 ml. Erlenmeyer flask and, after vigorous agitation, were allowed to stand overnight. The ethereal solution was removed by means of a separatory funnel and was dried over anhydrous magnesium sulfate. After filtration of the solution and evaporation of the ether, 24 g. of acidic material resulted. The product was soluble in glacial acetic acid in contrast to the insoluble nature of the parent Acintol P. Hydrogenations of this product in acetic acid solution using 0.10 g. PtO_2 were found to produce pressure drops of only 0.15 to 0.50 p.s.i. in the hydrogenation system.

A quantity of 50 g. of Acintol P was refluxed with 200 ml. of distilled glacial acetic acid. When cooled, the mixture separated into two liquid phases. A volume of 205 ml. of an acetic acid solution was removed by a separatory funnel. This was divided into two portions of equal volume. The first was hydrogenated using 0.10 g. PtO_2 and found to produce a pressure drop of 0.85 p.s.i. in 28 minutes. The other

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[1] See above, page 13.

portion was shaken for a period of two hours with five grams of Raney nickel. Ninety-five milliliters of the resulting solution was removed by decantation and was hydrogenated using 0.10 g. PtO_2 catalyst. This produced a pressure drop of 0.35 p.s.i.

A volume of 40 ml. of Acintol P, which undoubtedly contained some acetic acid, was found not to be dissolved by the acetic acid treatment mentioned above. This material was heated at reflux with 200 ml. methanol for one hour. The alcohol layer, which resulted after cooling, was removed and found to cause a drop of 0.35 p.s.i. pressure when hydrogenated using 0.10 g. PtO_2.

Apiezon-N

This high grade stopcock grease, manufactured by Metropolitan-Vickers Electrical Company, Ltd. and obtained from James C. Biddle Company, Philadelphia, Pa., was used as supplied in the preparation of gas chromatography column four.

Ascolube

A silicone stopcock grease supplied by Asco Manufacturing Company, Webster, N. Y., was used as received in the preparation of gas chromatography column five.

Benzene

Chemically Pure thiophene-free benzene was used without further purification.

Benzoic Acid

Standardization of the catalyst activity was accomplished by using

either the Mallinckrodt Analytical Reagent grade or Merck Reagent grade without further purification.

Carbon Disulfide

Reagent grade carbon disulfide was preferred for spectra determinations and was used after drying over silica gel.

Carbon Tetrachloride

This material also was used for spectra determinations and was dried over silica gel.

Catalysts

Three lots of Adams' platinum oxide catalyst were used in the course of this work. Lot A was obtained from J. Bishop and Company, Platinum Works, Malvern, Pa. and was designated by the manufacturers lot number 544. Lot B was manufactured by Baker and Company, Incorporated, (now Engelhard Industries, Incorporated). Lot C was manufactured by Engelhard Industries, Incorporated, 113 Astor Street, Newark 2, N. J. and specified as lot number 11.

Chloroform

Technical grade chloroform dried over silica gel was used in spectra determinations and in some of the chromatography experiments without purification.

Chromasorb P

This material is manufactured by Johns-Manville Company, 22 East 40th Street, New York 16, N.Y., and various samples having different particle sizes were used in the preparation of several of the gas chro-

matography columns.

Cyclohexane

Purification of ordinary solvent cyclohexane was accomplished using the method of Crowe and Smyth (26). The material boiled at 79.6° at a pressure of 737.5 mm. and had a refractive index of 1.4218 at 28.4° using sunlight.

Diazomethane

The method of DeBoer (27) was used for the preparation of diazomethane. The "Diazald" (N-methyl-N-nitroso-p-toluenesulfonamide) used in this preparation was obtained from Aldrich Chemical Company, Inc., 2369 North 29th Street, Milwaukee 10, Wisconsin.

Diethyl ether

Technical grade diethyl ether was used as obtained except when it was important to use dry ether. In these cases, approximately three liter quantities were dried in a dark brown bottle with sodium wire. The bottle was equipped with a calcium chloride drying tube.

2,2-Dimethoxypropane

A sample of 2,2-dimethoxy propane was obtained from Dow Chemical Company, Freeport, Texas, and distilled at 738.8 mm. pressure to give a fraction which boiled from 66.0-79.0°C.

Dow Corning High Vacuum Silicone Stopcock Grease

This material is manufactured by the Dow Corning Corporation,

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(26) R. Crowe and C. Smyth, J. Am. Chem. Soc., 73, 5407 (1951).

(27) T. DeBoer, Rec. trav. chim., 73, 229 (1954).

Midland, Michigan, and was used in preparing gas chromatography columns one and two.

Diamylamine

Two different grades of diamylamine were used. The first of these was white label grade supplied by Distillation Products, Industries, Rochester, N. Y. It was used without further purification. A less expensive material was diamylamine No. 1458 supplied by Sharples Chemical Division, Penn Salt Company, 3 Penn Center, Philadelphia 2, Pa., and was a mixture of isomeric diamylamines. It was purified by distilling a 450 ml. sample from 30 g. of granular zinc. The 366 ml. fraction boiling at 193° and 740 mm. pressure was used.

Diamylammonium Abietate

The method used for the preparation of this compound was identical to that used for the preparation of abietic acid. In the preparation of the free acid, the diamyl amine salt is produced as an intermediate. When used for the purpose of isolating pure diamylammonium abietate, only a slight modification of the procedure was necessary. The 228 g. of diamylammonium abietate produced in the former procedure was removed from the acetone solution by filtration. The crystalline product isolated in this manner was recrystallized twice from a mixture of 600 ml. of acetone and 330 ml. of 95 per cent ethanol to yield a product which weighed 140 g. after drying. The melting point was 140.0-140.2°, and the specific rotation was found to be -76.9° in absolute ethanol solution using the D line of sodium. The ultraviolet spectrum of the compound showed an absorption maximum at 241 mμ and had an extinction coefficient of 20,300.

7,8-Dihydroabietic Acid

The structure of this material was discussed by Royals (28), and the preparation was given by Kennedy (29). Into a three liter round bottomed three necked flask was placed 66.0 g. of diamylammonium abietate. The flask was equipped with a teflon stirring paddle powered with an electric motor, a dry ice-acetone condenser, and a second dry ice-acetone condenser connected to the flask through a two necked adapter. The second neck of the adapter was stoppered with a ground glass stopper. To the top exit tube of each condenser was fitted a length of rubber tubing. The tube from the first condenser was connected to a cylinder of ammonia gas while that from the second was connected to a manometer and a vacuum pump. The flask was suspended in a large pan filled with dry ice and acetone. The vacuum pump was utilized to evacuate the system and to maintain it under a slightly reduced pressure after it had been thoroughly flushed with ammonia gas. Ammonia gas was slowly admitted to the system and condensed until approximately 400 ml. of the liquid had collected. The system then was opened to the atmosphere by disconnecting the manometer connecting tube. At this time, 400 ml. of anhydrous ether was added carefully to the flask, and the cooling bath was removed. The stirring was begun and 10 g. of lithium metal was added slowly through the previously stoppered neck of the two necked adapter in small pieces measuring 0.5 in. by 0.25 in. cut from a strip of lithium ribbon. After addition of the metal was completed, the agitation of the contents of

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(28) Royals, op. cit., p. 151.

(29) R. Kennedy, A Study of the Structure of a 7,8-Dihydroabietic Acid, Unpublished Ph.D. Thesis, Emory University, 1956, p. 52.

the system was continued for one hour and 45 minutes. The cooling bath was returned to the flask, and 250 ml. of absolute ethanol was added slowly and cautiously from a dropping funnel fitted to the top of the two necked adapter. The cooling bath was removed and the contents of the flask were allowed to warm to room temperature. By means of a glas-col heating mantle, the excess ether and ammonia were evaporated from the system. Next, a mixture of 100 ml. of distilled water and 600 ml. of 95 per cent ethanol was added and, after acidification of the solution with dilute HCl and cooling with an ice-hydrochloric acid bath, a precipitate resulted. This solid was removed by filtration and washed with two portions of 500 ml. of distilled water. After drying overnight in the vacuum desiccator over sodium sulfate, the precipitate weighed 41.2 g. The solid was placed in a 500 ml. Erlenmeyer flask and dissolved in 250 ml. of acetone. After decolorization with carbon black and filtration, the solution was cooled slowly to room temperature and then placed in a refrigerator. Seven hours later, the crystals which were formed were separated from the solution by filtration and dried in the vacuum desiccator over sodium sulfate. The crystals weighed 20.3 g. and had a melting point of 173-176°.[1]

Ethanol

Both absolute and 95 per cent ethanol were used as obtained.

Hydrogen

The hydrogen gas was supplied in cylinders by the National Cylinder Gas Company, Atlanta, Ga., and was used without further purifi-

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[1]Reported: 173-181° without recrystallization.

cation.

Fully-Hydrogenated Abietic Acid and Its Methyl Ester

Four hydrogenation reaction runs were carried out using method one.[1] In each case, 9.14 g. diamylammonium abietate in 100 ml. glacial acetic acid was hydrogenated using 0.40 g. Adams' catalyst. The reaction was run overnight and the pressure decrease of the system corresponded to 2.01, 1.99, 1.88, and 2.11 moles of hydrogen absorbed per mole of acceptor for the four runs. In each of the four cases, the catalyst was removed by filtration, and the solution was forced in a thin stream into two liters of distilled water. The solution was decanted from the resulting precipitate, and the latter was washed with two liters of distilled water. After dissolving the solid in approximately 600 ml. diethyl ether, the resulting solution was dried over anhydrous sodium sulfate. The ethereal solutions of the four precipitates were filtered and combined, and after evaporation of the ether, 22.2 g. of solid remained.

One gram samples of the material were dissolved in 15 ml. of anhydrous diethyl ether in a 50 ml. Erlenmeyer flask and treated with an ether solution of diazomethane, dropwise, until the solution had a faint yellowish cast. The methyl ester of the fully-hydrogenated abietic acid in this ethereal solution was allowed to stand in the hood until most of the ether had been evaporated and then was warmed in a hot water bath to effect the removal of the remaining ether. These samples were used in the gas-liquid-partition chromatography experiments.

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[1]See below, page 78.

Half-Hydrogenated Abietic Acid and Its Methyl Ester

In a manner very much analogous to the above procedure, four hydrogenation runs were conducted using 9.14 g. diamylammonium abietate, 100 ml. glacial acetic acid, and 0.40 g. Adams' catalyst. In these runs, however, the shaking device was discontinued when the pressure of the hydrogen had decreased an amount corresponding to 1.35 moles of hydrogen per mole of acceptor. The catalyst was removed from the solution by filtration through a sintered glass funnel, and the solution was forced in a fine jet into three liters of water by means of a pipette. The aqueous solution which resulted was decanted from the precipitate, the solid washed with three two liter portions of distilled water, and dissolved in one liter of diethyl ether. Drying of the ethereal solution was accomplished by allowing it to stand over anhydrous sodium sulfate which was later removed by filtration. The ether was boiled off on the steam bath using the water aspirator to decrease the boiling point. A yield of 23.2 g. half-hydrogenated abietic acid was obtained.

One gram samples of this solid were esterified in the exact manner as that used for the preparation of the methyl ester of fully-hydrogenated abietic acid.

Methanol, Anhydrous

A quantity of 1500 ml. of commercial absolute methanol was placed in a two liter round bottomed flask with 15 g. of magnesium ribbon. The vessel was equipped with a Friedrichs reflux condenser and a drying tube containing "Drierite". The mixture was allowed to stand overnight as the reaction proceeded. After this, the flask was fitted with a glas-col

heating mantel and brought to reflux for two and one-half hours. The methanol was then distilled rapidly through the Todd column.

Methyl Abietate

This material was prepared in a manner exactly analogous to the preparation of the methyl esters of half- and fully-hydrogenated abietic acid.

Methyl Esters of the Acids of Acintol FA 2

Acintol FA 2 was subjected to conventional esterification conditions by dissolving 150 g. of the material in 600 ml. of anhydrous methanol in a one liter round bottomed flask. Eight milliliters of concentrated sulfuric acid was added, and the contents of the flask were then heated under reflux for 17 hours. The warm solution was poured into 2500 ml. of water containing 25 g. of sodium chloride, and the mixture then was extracted with three 500 ml. portions of diethyl ether. The combined ether extracts themselves were washed with two 1000 ml. portions of water. The ether solution of the esterified mixture of acids of Acintol FA 2 was placed in a 1500 ml. flask with 300 g. of hydroxyl phase Dowex 3 resin (33% water, exchange capacity 2.1 meq./g., dry) and allowed to remain in contact with the resin at room temperature for three hours. The resin was removed by filtration and washed with 200 ml. diethyl ether. Sodium sulfate was used to dry the combined ethereal solutions. After removal of the drying agent by filtration and evaporation of the ether from the esters by using a water aspirator and steam bath, 143 g. of the esters of Acintol FA 2 remained. The infrared spectrum of this material showed the presence of a carbonyl absorption at 5.74 μ.

Methyl Oleate

The method of Lorette and Brown (30) was used for the esterification of oleic acid. The resulting methyl oleate was distilled through a Vigreux column in the Todd distillation apparatus. The fraction boiling from 147-160° at one millimeter pressure was collected for redistillation. The redistillation yielded a fraction boiling at 163.8-167.0° at one millimeter which weighed 147.0 g. The infrared spectrum of this material showed the presence of a carbonyl absorption at 5.75 μ.

Methyl Stearate

Eight grams of Matheson, Coleman, and Bell technical grade stearic acid was placed in a 250 ml. Florence flask attached to a reflux condenser. A quantity of 150 ml. of absolute methanol was added followed by 0.2 ml. concentrated sulfuric acid. The solution then was heated one hour and 15 minutes under reflux. The solution, while still hot, was rapidly poured into one liter of distilled water. Vigorous shaking of the resulting mixture, followed by extraction with 300 ml. diethyl ether yielded an ethereal solution of the methyl stearate. This solution was extracted three times with 200 ml. quantities of 5 per cent potassium hydroxide solution and then by 300 ml. of distilled water. The ether solution was dried with anhydrous sodium sulfate, the drying agent removed by filtration, and the solvent evaporated on the steam bath and water aspirator to yield 8.2 g. of methyl stearate.

Micro Beads

These beads were of glass and were 50/80 mesh in size. They

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(30) N. Lorette and J. Brown, Jr., J. Org. Chem., 24, 261 (1959).

were manufactured by Microbeads, Incorporated.

Oleic Acid

Baker U.S.P. oleic acid was fractionated at reduced pressure through the Todd column with great difficulty due to its high boiling point even at five millimeters pressure. The distillate which boiled over a temperature range of 203.5-214.5° at approximately five millimeters was collected for use. Pressure fluctuations were apparently responsible for the wide boiling point range.

Silicon Gum SE 30

Gas chromatography column six was prepared using this material which is manufactured by General Electric Company, Silicon Products Department, Waterford, N. Y.

Tall Oil Rosin

Industrial Chemical Sales Division of West Virginia Pulp and Paper Company, 230 Park Avenue, New York 17, N. Y., supplied several samples of Tall Oil Rosin which was used in this work. Complete specifications were not available, but the rosin was known to contain a maximum of 5 per cent fatty acids. The solid material was translucent and had a light amber color. Although for the most part the samples were homogeneous, in some there were found small spots of an opaque soft waxy material which had a light yellow color. The bulk of the sample was a hard, brittle, amber colored material. The spots of waxy material were removed manually before the rosin was used in the hydrogenation experiments and before it was used in the preparation of abietic acid or diamylammonium abietate.

Tetrahydrofuran

This material was purified by distillation from potassium metal according to the method of Grovenstein and Williams (31).[1]

2,2,4-Trimethylpentane

Technical grade 2,2,4-trimethylpentane as supplied by Distillation Products Industries, Rochester, N. Y., was distilled to remove high-boiling materials and non-volatile contaminants. The resulting solvent was used in the preparation of packing materials for some of the gas chromatography columns.

Hydrogenation Techniques

Hydrogenation Method One

Most of the hydrogenation experiments were conducted using this method. The material to be hydrogenated was either weighed and placed in a hydrogenation bottle along with the desired volume of solvent, or a solution of known concentration of the material was prepared and an aliquot portion placed in the hydrogenation bottle. The desired quantity of Adams' platinum catalyst was weighed and quantitatively transferred to the reaction bottle. The container was assembled on the standard Parr Low Pressure Reaction Apparatus and evacuated until the solvent was caused to boil. Hydrogen was next admitted to the reaction vessel at approximately 50 p.s.i. Again the system was evacuated. This was repeated two additional times for the purpose of removing any air in the

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(31) E. Grovenstein, Jr. and L. Williams, Jr., J. Am. Chem. Soc., 83, 414 (1961).

[1]The author is grateful to Laney P. Williams, Jr., who purified this material.

hydrogenation bottle or in its contents. When this operation was complete, hydrogen was admitted at the desired initial pressure (usually 50.0 p.s.i. gauge pressure or approximately 64.5 p.s.i. absolute pressure). After allowing the apparatus a few minutes to reach thermal equilibrium, the temperature of the hydrogen tank, the gauge pressure, and the barometric pressure were recorded.

The reaction was started by beginning the shaking device of the apparatus and simultaneously starting a stopwatch. As the reaction proceeded, the time lapse and the pressure of the system were read and recorded at regular intervals. The rate of pressure decrease of the system determined the length of the time intervals which were used in each reaction. These varied from 15 seconds in the case of the tall oil fatty acid fractions to 120 seconds in the case of the benzoic acid standardization reactions.

When it was desired to discontinue the reaction, whether this was at total or only partial hydrogenation of the substrate, the shaking device was stopped, the hydrogen tank was closed off from the reaction container, and the hydrogen remaining in the bottle was removed by evacuation of the system. Air was then readmitted, and the reaction vessel removed. The catalyst was separated from the solution by filtration through a sintered glass filter.

Hydrogenation Method Two

When it was desired to conduct the hydrogenation at constant temperature, the method given above was altered slightly. A copper jacket was added which surrounded the reaction vessel. After the reaction components had been placed in the bottle, water of a predetermined constant

temperature was circulated through the jacket. When the temperature of the contents of the vessel had reached the same temperature as the circulating water, the apparatus was assembled and hydrogenation method one was followed.

This technique was used mainly in the determination of the rate constant values necessary for evaluating the energy of activation for abietic acid. The experiments which were conducted using this technique were runs 1, 2, 10, 13, 14, 19, 20, 26, and 28-47 in which diamylammonium abietate was hydrogenated.[1]

Hydrogenation Method Three

When it was inconvenient to use a constant temperature bath to maintain the reaction bottle at a given temperature, but it was desired to minimize thermal effects due to differences in temperature of the reaction and its surroundings, the room temperature was deliberately adjusted. During the colder parts of the year, this technique could be used over a wide temperature range. By turning off the heat, opening the windows of the room, and allowing the room to remain this way overnight, it was possible to bring the temperature down as low as 16.0°. On the other hand, by keeping the room tightly closed, and heating it with gas flames as well as the steam radiator operating at maximum capacity, it was possible to bring the temperature up as high as 33.9°. This slight alteration from method one was used in all of the runs in the hydrogenation of methyl oleate.

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[1]See above, page 38.

Isomerization Experiments in the Hydrogenation of Abietic Acid

Partial Hydrogenation of Abietic Acid

Two hundredths of a mole of diamylammonium abietate was hydrogenated for two minutes with 0.40 g. Adams' catalyst in 100 ml. glacial acetic acid and then discontinued. The hydrogenation solution was freed from the catalyst by filtration. The product was isolated by diluting the hydrogenation solution with distilled water until precipitation was complete, decanting the solution from the solid, washing the solid, and then recrystallizing it from 80 per cent aqueous acetone. Upon cooling, crystals formed which were removed from the solvent by filtration. After drying overnight in a vacuum desiccator over sodium sulfate, these crystals melted at 137-146°. The solid showed an absorption maximum at 241 mμ in the ultraviolet spectrum and an extinction coefficient of 6,210. Assuming that the hydrogenated constituents do not absorb at this wave length, this represents 25.6 per cent abietic acid present.

Non-Poisoning of the Catalyst Surface in the Hydrogenation of Abietic Acid

Two hundredths of a mole of diamylammonium abietate was hydrogenated with 0.40 g. Adams' catalyst in 100 ml. glacial acetic acid for 2.25 minutes. This produced an absorption of 0.0222 moles of hydrogen. The hydrogenation was discontinued, the catalyst removed and replaced with fresh catalyst, and the hydrogenation resumed at the last recorded pressure. The data was plotted and the graph obtained indicated no change in the hydrogenation process from that found when diamylammonium abietate was hydrogenated to completion without discontinuing

the reaction. Therefore, catalyst poisoning is probably not responsible for the three phases of the hydrogenation found for diamylammonium abietate as described on page 43 .

Decrease in Rate Constant Due to Pre-adsorption of Substrate on the Catalyst Surface

Four-tenths gram of Adams' catalyst was placed in a hydrogenation bottle with 50 ml. glacial acetic acid. The catalyst was reduced to platinum by shaking the mixture with hydrogen on the reaction apparatus. The bottle was evacuated, air was readmitted, and a solution of 50 ml. glacial acetic acid containing 9.14 g. diamylammonium abietate was added. The bottle was evacuated and filled with hydrogen and then re-evacuated. (This process was repeated two times.) The shaker then was begun, and the mixture was allowed to shake in the absence of hydrogen for 15 minutes. Hydrogen gas was admitted, and the hydrogenation reaction commenced. The data obtained from two runs exactly like this yielded initial rate constants of 84.1 and 87.3 x 10^{-4} $min.^{-1}/g.$ at 31.8°C and 31.1°C respectively.

Non-Isomerization of the Substrate on the Unreduced Catalyst Surface or by the Solvent

A quantity of 0.02 moles of diamylammonium abietate, 0.40 g. Adams' catalyst, and 100 ml. glacial acetic acid was placed in a hydrogenation bottle which then was evacuated and shaken for 15 minutes. After this, the bottle was filled with hydrogen and hydrogenation was begun. The initial rate constant was found to be 414 x 10^{-4} $min.^{-1}/g.$ and the final rate constant was found to be 10.8 x 10^{-4} $min.^{-1}/g.$ at 31.7°C. This is

in agreement with the usual results obtained from standard experiments reported in this work.

Non-Isomerization of the Substrate on the Reduced Catalyst Surface

Fifty milliliters of glacial acetic acid was shaken with 0.04 g. Adams' catalyst in the presence of hydrogen for 15 minutes. Then 50 ml. glacial acetic acid containing 0.02 moles diamylammonium abietate was added to the bottle. The bottle was evacuated, filled with hydrogen, and re-evacuated three times. The shaker was started and continued for 15 minutes. The apparatus then was disassembled, the catalyst was removed from the solution by filtration, and the solution was replaced in the hydrogenation bottle. Four-tenths gram of fresh Adams' catalyst was added to the bottle, and hydrogenation carried out using method one. The initial rate constant obtained was $516 \times 10^{-4} \text{min.}^{-1}/\text{g.}$, while the final rate was $12 \times 10^{-4} \text{min.}^{-1}/\text{g.}$ at 31.4°C. This shows that the two rate constants discussed on page 43 are not produced by isomerization of the abietic acid on the catalyst surface.

Other evidence similar to this was obtained as follows: two grams of abietic acid was dissolved in 25 ml. of dry chloroform. Twenty milliliters of this solution was shaken with 0.6 g. reduced PtO_2 in a 50 ml. volumetric flask overnight. Infrared spectra were made of the original solution and of that which had been treated with platinum. They were found to be identical.

Effect of Heat on the Half-Hydrogenated Abietic Acid

Eighteen grams of half-hydrogenated abietic acid was dissolved in one liter of diethyl ether and washed with two portions of two liters of

distilled water. The ethereal solution was dried with anhydrous sodium sulfate. Following filtration to remove the drying agent, the ether was evaporated on the steam bath under water aspirator pressure from a two liter boiling flask equipped with Claisen head, water cooled condenser, receiver, and vacuum adapter. To the gummy residue 150 ml. of acetone was added, and the whole brought to boil under a reflux condenser, then cooled, and filtered into a 250 ml. round bottomed flask. Much of the solvent was evaporated on the steam bath with aid of the water aspirator, and when the volume was about 30 ml., the solution was seeded with a few crystals of fully-hydrogenated abietic acid and diluted with 25 ml. acetone to cause the crystallization of the dissolved resin acid. Upon filtering, the mixture left a residue which was dried in the vacuum desiccator overnight over sodium sulfate. The product then weighed 7.1 g. and melted from 125-130°. A one per cent solution of the solid in absolute ethanol gave a specific rotation at 21° using the sodium D line of +10.2°.

A sample of 0.4971 g. of the above material was vacuum sublimed in a conventional apparatus. At a pressure of 15 microns and a temperature of 136.0°, the material began to sublime and 23 minutes later and a material (0.3044 g.) melting at 72-85° was recovered from the condenser. The infrared spectrum of this material was not significantly different from that of the starting material. Another quantity of 0.168 g. which did not sublime was recovered, and it had a melting point of 78-84°.

A quantity of the half-hydrogenated abietic acid having a melting point of 125-130° was placed in a melting point tube and heated in a melting point bath for two and one half hours at 100°. The melting point was subsequently determined to be 120-130°.

Another amount of the half-hydrogenated resin acid (0.400 g.) was dissolved in 10 ml. distilled toluene and heated at reflux for one and one half hours. Twenty milliliters of absolute methanol was added and the solvents azeotropically distilled at 64°. Thirty milliliters of water was added to precipitate the solid. After the water was decanted and the solid washed with an additional 30 ml. portion of water, the solid was dissolved in acetone and filtered. The filtrate was evaporated to a total volume of seven milliliters. Five-tenths milliliters of water was added and the flask allowed to stand for 12 days. The crystals were removed by filtration and when dried were found to have a melting point of 157-164°.

Activity Relationships of Catalyst Lots

Standardization of Catalyst Lot A

In order to permit the comparison of this work with that of others, catalyst lot A was standardized by the hydrogenation of benzoic acid in glacial acetic acid. A sample of 2.44 g. or 0.02 moles of benzoic acid was introduced into 50 ml. of acetic acid and hydrogenated according to method one using 0.10 g. of the catalyst. The rate constant for the reaction, which was first order with respect to hydrogen, was found to be 285 x 10^{-4} $min.^{-1}$ per g. of catalyst at a temperature of 31.0°. The cyclohexanecarboxylic acid which was produced was not isolated.

Comparison of Catalyst Lots

The three lots of catalysts were standardized with respect to each other by comparing the results of several hydrogenation runs made using the various lots of catalyst in the hydrogenation of Acintol FA 2.

The same technique was used in the hydrogenation of diamylammonium abietate. This permitted the rate constants obtained for a given substrate using different lots of catalyst to be corrected to the activity of only one catalyst lot.

Catalyst Lots A and C in the hydrogenation of Acintol FA 2.--In the hydrogenation of Acintol FA 2 only catalyst lots A and C were used. The average rate constant value at 25° of five hydrogenation runs using lot C was found to be 0.2055 $min.^{-1}/g.$ Lot A was considerably more active in the hydrogenation of Acintol FA 2 and yielded an average value of 0.2743 $min.^{-1}/g.$ for four runs at 25° using the same amount of acceptor (6.00 g. in 100 ml. glacial acetic acid solution). Corrections were made on the basis of the following relationship:

$$\frac{\text{Rate Constant for Catalyst Lot A}}{\text{Rate Constant for Catalyst Lot C}} = \frac{0.2743}{0.2055} = 1.335$$

Catalyst Lots A, B, and C in the hydrogenation of diamylammonium abietate.--Hydrogenation runs were conducted for diamylammonium abietate using all three lots of catalyst. The activity of lots A and B were found to be very nearly equal; the former was only slightly greater. The hydrogenations were conducted at 27.5° using 9.14 g. diamylammonium abietate and 0.40 g. of the catalyst in 100 ml. glacial acetic acid solution. Hydrogenation method one yielded an average rate constant value for lot B of 0.0313 $min.^{-1}/g.$ for four runs, while a value of 0.0336 $min.^{-1}/g.$ was found to be the average rate constant of lot A for five hydrogenation experiments.

$$\frac{\text{Rate Constant for Catalyst Lot A}}{\text{Rate Constant for Catalyst Lot B}} = \frac{0.0336}{0.0313} = 1.07$$

Catalyst lots C and B were compared at 25°C, otherwise using the

same conditions as above. The average rate constant value of 0.0190 $min.^{-1}/g.$ for eight runs using lot C is compared to the value of 0.0332 $min.^{-1}/g.$ obtained as average for 16 runs using catalyst lot B.

$$\frac{\text{Rate Constant for Catalyst Lot B}}{\text{Rate Constant for Catalyst Lot C}} = \frac{0.0332}{0.0190} = 1.75$$

Treatment of Data

Calculation of the Reaction Rate Constant

It is frequently found that catalytic hydrogenation reactions are first order with respect to hydrogen (32). Thus, if a hydrogenation reaction apparatus which has constant volume is used, and if the apparatus is equipped with a suitable pressure gauge, the progression of the reaction with time may be followed by observing the decrease in hydrogen pressure. This is the type of apparatus which has been used in the present study, and all of the rate constants presented herein have been determined by following the pressure of the system with time.

Chemical reactions which are first order with respect to a particular reactant may be described by the following equation:

$$-\frac{dc}{dt} = kc,$$

where c represents the concentration of the reactant, t represents time, and k is the reaction rate constant. In a catalytic hydrogenation reaction first order with respect to hydrogen, the concentration of hydrogen would be proportional to the pressure of the hydrogen, assuming

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(32) K. Laidler in Catalysis, Vol. I, edited by P. Emmett, Reinhold Publishing Corporation, 1954, pp. 121-122.

the reaction was conducted in a constant volume system. The above equation could then be rewritten as follows:

$$-\frac{dP}{dt} = kP,$$

where P represents the pressure of hydrogen in the reaction system. Integration of this equation between the limits of t = zero and t = t yields the following expression:

$$\log \frac{P_0}{P_t} = \frac{kt}{2.303},$$

where P_0 is the initial pressure of hydrogen in the system and P_t is the pressure of hydrogen at time t. This is the equation which has been used in the present study to obtain values for k which are representations of the rate constants for the various reaction conditions investigated.

The data obtained in the hydrogenation experiments as described[1] were used to evaluate the rate constant of the particular run. To accomplish this, the values of time in minutes were plotted as absissas, while those of log P_0/P_t were plotted as ordinates. The product of 2.203 and the slope of the straight line which resulted was divided by the weight in grams of the catalyst used to yield the value of the rate constant in units of $min.^{-1}$ per g. A typical plot is shown in Figure 8, page 89.

Evaluation of the Apparent Activation Energies

The rate constants derived according to the above procedure at different temperatures for a given hydrogen acceptor were used to

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[1]See above, page 78.

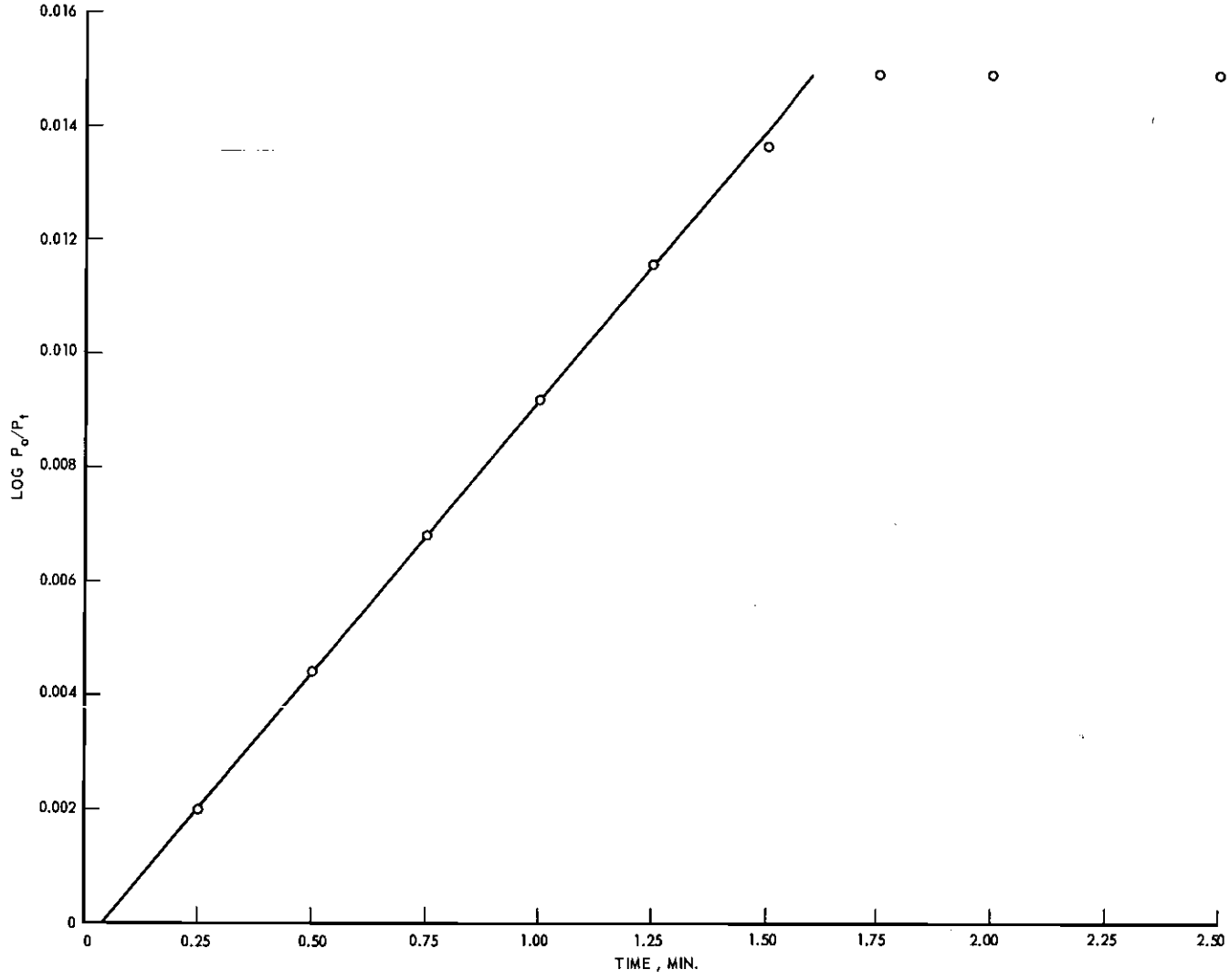

Figure 8. Typical Plot of Log P_o/P_t Against Time in the Hydrogenation of Acintol FA 2.

evaluate the apparent activation energy of the hydrogenation of the particular substrate. This was accomplished through the use of the Arrhenius law which is given by the following equation:

$$\frac{d(\ln k)}{dT} = \frac{E_a}{RT^2} .$$

Upon integration and conversion to common logarithms this yields

$$\log k = - \frac{E_a}{2.303\ RT} + c ,$$

where k is the reaction rate constant, c is the integration constant, R is the gas constant, T is the absolute temperature at which the rate constant is determined, and E_a is the apparent activation energy.

This term is called the apparent activation energy because it is in reality not the activation energy of the reaction but the summation of several factors: the heat involved in the adsorption of the acceptor and in the adsorption of hydrogen, and the activation energy of the combination of the acceptor and the hydrogen would all appear in E_a (33).

In order to use the Arrhenius law to determine the apparent activation energies in this work, values of log k/g. were plotted as ordinates against the reciprocals of the absolute temperature as absissas. The slope of the resulting straight line was equal to $-E_a/2.303R$.

The usefulness of the values obtained using this method is not in the exactness of what is being measured, but rather it is in the application of this value in correcting to another temperature a reaction rate constant at some measured temperature. These corrections were

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(33) Ibid., pp. 135-137.

made so that the reaction rate constants obtained under varying temperatures might be compared at a standard temperature. An equation which is a variation of the above expression was used for purposes of making the corrections.

$$\log \frac{k_1}{k_2} = - \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Correction of Rate Constant Values for Differences in Hydrogenation System Volume

Since most of the hydrogenations were conducted in the larger hydrogenation bottles, but some were carried out using smaller bottles, it was necessary to correct the rate constant values for the latter to the values which would have been obtained if the larger containers had been utilized in these experiments. The total volume of the hydrogenation apparatus using the smaller bottles was 4.430 l., while the total volume of the system with the larger bottles was 4.484 l. All rate constant values reported herein are corrected to the larger volume system by the following relationship:

$$k_{4.484 \text{ l. system}} = k_{4.430 \text{ l. system}} \times \frac{4.430}{4.484}$$

In order to compare the results of this work to that of other workers, the rate constants should be multiplied by the volume of the hydrogenation system, 4.484 l. (34).

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(34) H. Smith, W. Bedoit, Jr., and J. Fuzek, J. Am. Chem. Soc., 71, 3769 (1949).

Calculation of the Reaction Mixture Temperature at Completion of the Reaction

In some runs, the temperature change during the reaction was so great, it was desirable to calculate the reaction mixture temperature at completion of the reaction, so that the mean temperature might be found. The mean temperature was then used in the determination of the apparent activation energy for the reaction, by assuming that to be the temperature at which the reaction was conducted. In order to calculate the reaction mixture temperature, use was made of Newton's law of cooling (35). According to this law, the rate of cooling of a body having a temperature higher than that of its surroundings is represented by the following equation:

$$\frac{dT}{dt} = - k(T_o - T_{rm}) ,$$

where T_o is the temperature of the body, T_{rm} is the temperature of the surroundings or room as in this case, k is a constant dependent upon the specific heat of the body, and t is the time. Integration of the equation and conversion to base 10 logarithms gives the following relationship:

$$\log \frac{T_t - T_{rm}}{T_o - T_{rm}} = - \frac{bt}{2.303} ,$$

where T_o is the initial temperature of the body, and T_t is its temperature at time t.

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(35) L. Smail, Calculus, Appleton-Century-Crofts, New York, N.Y., 1949, p. 272.

The value for the constant b can be determined by plotting the logarithm of the temperature terms indicated by the left side of the equation against time. The slope of the straight line which results is equal to - b/2.303. This has been done in the case of the hydrogenation of Acintol FA 2, and the constant in conjunction with the above equation has been used to calculate the temperature of the reaction mixtures at the time at which the reactions were completed.

Chromatography Experiments

Attempted Separation of Hydrogenated Abietic Acid by Elution Chromatography

Half-hydrogenated abietic acid having a melting point of 115-140° was passed through a chromatography column as follows: The column was prepared by making a slurry of 200 g. of silicic acid in 400 ml. chloroform. A glass column having a diameter of two inches and a height of two feet which was equipped at the bottom with a medium sintered glass disk was packed with the slurry, and the solvent was allowed to drain from the column until no more solvent dripped from the column. A solution of 17.5 g. of the half-hydrogenated abietic acid in 20 ml. of chloroform was placed carefully on the silicic acid column. The solvent was allowed to soak into the column, and a few additional milliliters of chloroform was added to help wash the hydrogenated material onto the column. The column then was filled with chloroform, and a flask was placed under the column to receive the eluent. After about 700 ml. of eluent was collected, it was transferred to a one liter boiling flask and evaporated on the steam bath under water aspirator pressure. When the volume of

the solution was about 200 ml., it was filtered through a funnel containing glass wool into a 300 ml. boiling flask, and the evaporation was continued until all the solvent had been removed. The residue was dissolved in 20 ml. boiling acetone then refrigerated. A crystalline residue was obtained, which when removed and dried weighed 7.63 g. and melted at 145-155°.

This sample of partially purified, half-hydrogenated abietic acid was subjected to other chromatographic techniques. A chromatography column of about one inch diameter and four feet long and equipped at the bottom with a stopcock for starting and stopping the flow of solvent was placed in an upright position. About 20 ml. of thiophene-free benzene was placed in the column and a piece of glass wool was inserted into the tube and forced to the bottom by means of a glass rod. A quantity of Berkshire sand was poured into the column through a funnel until it filled the column for a length of about two centimeters. The column was then filled with benzene to within about 25 cm. of the top. Through a small funnel, 241.4 g. of alumina was added. This was done slowly and in a fine stream to allow the column to be packed by the force of gravity. When the column was filled, another small amount of Berkshire sand was added to the top of the column. Approximately 100 ml. of benzene was allowed to flow through the column. When this was completed, a solution of 3.001 g. of the sample in 10 ml. benzene was carefully placed on the column head by means of a pipette. The column was closed at the top by means of a stopper fitted with a Y tube. The Y tube was connected to suitable containers which permitted the method of gradient elution to be used in developing the column (36). In this work, the gradient

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(36) R. Williams, Analyst, 77, 905 (1952).

elution apparatus consisted of two conical-shaped glass containers of one liter capacity. These containers were identical; they were of the same volume, had walls which sloped at the same angle, and had a small opening at both their bases and their points. One of the these containers filled with dry thiophene-free benzene was suspended point down and was attached through the opening in its point to one of the arms of the Y tube which was closed by a stopcock. The other container filled with 40 per cent dry ether in dry thiophene-free benzene was suspended base down and was attached through the opening in its base to the last arm of the Y tube which was also closed by a stopcock. Both containers were at the same height above the chromatography column.

When it was desired to begin the development, the stopcocks of the Y tube were opened allowing the solvents to flow simultaneously into the alumina column. Fifteen milliliter fractions were collected from the column, and then transferred to 50 ml. Erlenmeyer flasks from which the solvent was removed on the steam bath. Ninety two fractions were so collected and treated. The first 47 fractions contained less than 0.01 g. of residue each. The weights of the fractions 48 through 92, however, were considerably larger, with most of them containing 0.05 to 0.07 g. of residue. There was no significant variation between the weights of these fractions, indicating that adequate separation had not been achieved. Melting points of selected fractions are listed here: Fraction 48, m.p. 169-171°, Fraction 51, m.p. 168-170°, Fraction 53, m.p. 164-167°, Fraction 55, m.p. 163-165°. The higher numbered fractions had lower melting points, and there were no others that had less than a six degree melting point range. The infrared spectra of several representative fractions were not noticeably different.

Attempted Separation of Hydrogenated Abietic Acid with Paper Chromatography

Four strips of chromatography paper were spotted with a solution of the partially purified half-hydrogenated abietic acid in chloroform. Two of these strips then were placed in chromatography jars and suspended in 90 per cent acetone. The two others were suspended in jars containing 90 per cent ethanol. Three hours were required for the solvent to reach the top of the strips in the former cases and four hours in the latter two cases. After the strips were removed, dried, and painted with a 0.4 per cent solution of bromthymol blue in ethylene glycol-monomethyl ether, there was no indication of any separation of the components of the resin acid mixture.

Attempted Separation of Hydrogenated Abietic Acid with Gas Chromatography

A Perkin-Elmer Vapor Fractometer Model 154D was utilized under a number of different conditions in an attempt to separate the components of the mixture obtained by the half hydrogenation or the complete hydrogenation of abietic acid. The products were methylated with diazomethane prior to the attempted separation. These experiments did not yield data suitable for the quantitative analysis of the mixtures, nor were the results encouraging enough to lead one to think that improvement could be made while using the presently available equipment. It appears that in all probability the thermal limit of the Perkin-Elmer instrument is too low to effect separation of these materials, or the detector is too insensitive at the high temperatures involved.

Thermistors were used in the thermal conductivity cell as the detector. Helium was used as the carried gas, and the samples were

placed in the flash evaporator in benzene solution.

Gas Chromatography Columns.--Two of the columns investigated were supplied by Perkin-Elmer Instrument Company. The others were made during the course of this work.

Perkin-Elmer OX column.--Two meters in length, made of 1/4 in. O.D. stainless steel tubing packed with diatomaceous earth, supporting silicone grease.

Perkin-Elmer RX column.--Three meters long, made of 1/4 in. O.D. stainless steel tubing packed with diatomaceous earth, supporting polypropylene glycol (UCON LB-550-X).

Column One.--A three meter length of 1/4 in. O.D. copper tubing packed with 60/80 mesh unactivated Chromasorb (Perkin-Elmer No. 154-0318) supporting 20 per cent Dow-Corning High Vacuum Silicone Stopcock Grease by weight.

Column Two.--A three meter length of 1/4 in. O.D. copper tubing packed with 30/60 Chromasorb P, supporting 20 per cent Dow-Corning High Vacuum Silicone Stopcock Grease by weight.

Column Three.--Column one and column two joined together by means of a suitable connecting unit.

Column Four.--A three meter length of 1/4 in. O.D. copper tubing packed with 50/80 mesh Micro Beads, supporting 0.20 per cent Apiezon-N stopcock grease by weight.

Column Five.--A 2.7 m. length of 1/4 in. O.D. copper tubing packed with 50/80 mesh Micro Beads, supporting 0.061 per cent Ascolube silicone stopcock grease by weight.

Column Six.--Six feet long, made of 1/4 in. O.D. copper tubing

packed with 70/170 mesh acid and base washed Chromasorb P, supporting approximately 2 per cent SE 30 silicon gum.

Method of preparation of the columns.--All columns made in the course of this work were packed by the same method. The length of tubing to be used was cut from ordinary 1/4 in. O.D. copper tubing. A small glass wool plug about the size of a match head was placed in one end of the copper tube. After this end was covered with a rubber dropper bulb, the column was placed upright. A small funnel was attached to the open end of the tube by means of a piece of Tygon tubing, and the packing was slowly poured into the funnel, and ultimately, into the tubing. As this operation was done, an assistant was required to tap the sides of the tubing constantly and rapidly with an ordinary laboratory metal ring through which the tube was inserted. The tapping was begun at the bottom of the column and gradually was moved up the column to the top. When the top was reached, the ring was returned to the bottom of the column and the process repeated. This was continued as more packing material was added until the tubing was completely filled. This operation normally required 30 minutes. The funnel was then removed, and a very small amount of the packing was removed from the top end of the tube and replaced by another glass wool plug of the same size as that used at the bottom.

Preparation of column packing materials.--The packing materials used in columns one through five were all prepared in essentially identical manners. The components varied, but the technique used was the same and will be only generally discussed.

The desired weight of the supporting agent (e.g., 40 g. Chromasorb) was placed in a one liter round bottomed flask. The flask had been

altered by making three depressions in the walls which acted as paddles as the flask was revolved. The depressions were approximately one inch deep, about 3/8 in. wide, were approximately equa-distance from each other and were made at an angle of 60-70° from the horizontal when the flask was upright. A solution of the liquid phase (e.g., 10 g. silicone stopcock grease) was made by dissolving the appropriate weight of the liquid phase in about 400 ml. of a suitable solvent, normally 2,2,4-trimethylpentane. The mixture was then placed on the Rotovap over the steam bath to remove the solvent and to give a uniform coating of the liquid phase on the supporting agent.

The packing material used in the preparation of column six was made according to the method of Vanden Heuvel, Sweeley, and Horning (37).[1] Thirty-six grams of Chromasorb P, 60/80 mesh (P.E. No. 154-3018) was placed in a 400 ml. beaker and washed under constant stirring at room temperature with 144 ml. of 12 N hydrochloric acid for four hours. The acid was decanted and discarded. The material was then washed with distilled water until the washings were acid free as evidenced by their effect upon litmus paper. The solid was then removed by filtration and dried in an oven at 100°. The cooled Chromasorb was suspended in a solution of 10.1 g. of potassium hydroxide in 360 ml. absolute methanol. Constant agitation was maintained by the magnetic stirrer and after stirring for four hours, the solvent was decanted and the residue washed with methanol until the washings were neutral to litmus. The material

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(37) W. Vanden Heuvel, C. Sweeley, and E. Horning, J. Am. Chem. Soc., 82, 3481 (1960).

[1]The method was supplied by Dr. C. C. Sweeley of the University of Pittsburg.

was removed by filtration and dried overnight in the oven at 100°. The Chromasorb was cooled and resieved to obtain 23.5 g. of 70/170 mesh product.

This Chromasorb was stirred with a solution of 3.0 g. SE 30 silicone gum in 100 ml. toluene for five minutes and quickly filtered through a course, sintered glass funnel. Air was drawn over the residue for 10 minutes and the residue then dried in an oven on a porous plate for 1.75 hours to give a yield of 24.8 g. of column packing.

Identification of the Product of Hydrogenation of Methyl Oleate and Methylated Acintol FA 2 by Gas Chromatography

The products of the hydrogenation of both methyl oleate and esterified Acintol FA 2 were shown to be principally methyl stearate by the comparison of gas chromatograms (made under identical conditions) of these materials with that of an authentic sample of methyl stearate. The chromatograms were obtained through the use of the Perkin-Elmer OX column.

CHAPTER IV

RECOMMENDATIONS

The fact that abietic acid is hydrogenated in a two step reaction, apparently first to a dihydroabietic acid, followed by its subsequent reduction to a tetrahydroabietic acid, offers many possibilities for further extension of this research. It is imperative, however, that some method be discovered either which permits the analysis of the number of components in the mixture of products from the hydrogenation reaction and their relative percentages present or which permits at least the separation of the major constituents of the mixture from the less important components.

It is, therefore, recommended that a research program be undertaken to find a suitable analytical or separatory tool. It would appear that perhaps the most promising path to pursue would be the comprehensive examination of various chromatographic techniques, especially gas chromatography. While during the course of this work, very little encouraging results were obtained using gas chromatographic techniques, it is thought that if an instrument were available which had a higher thermal capacity, and/or a more sensitive detector, that separation might be more easily achieved.

It certainly is not unreasonable to think that the various isomeric materials produced by not only half hydrogenation of abietic acid but full hydrogenation of the material could be separated using gas chromatography, if the proper conditions and equipment were chosen.

Horning (38) et al, have effected the separation of certain steroidal compounds which varied only in the stereochemistry of the ring fusions of the A and B rings. These materials have considerably higher molecular weights than the resin acids and consequently should be much less volatile.

Another approach which might be attempted toward the separation of the mixtures would be through an exhaustive study of the solubility characteristics of a large number of amine salts of the acids. Similar studies have led to the selective separation of naturally occurring resin acids, such as in the preparation of abietic acid, if the proper amine and solvent can be found.

If a preparative method of separation could be found, such as the one just proposed or perhaps even an elution chromatographic technique, it would be of considerable interest to attempt to elucidate the structure of the dihydroabietic acids formed in the hydrogenation of the parent acid using various catalysts and solvents, if indeed they are different. It would also be of interest to know something about the stereochemistry of the tetrahydroabietic acids which are formed on hydrogenation under varying conditions.

It is also proposed that the various dihydroabietic acids which have been previously reported as pure compounds, whether they resulted from hydrogenation of abietic acid or from some other source, be prepared and hydrogenated further under the conditions used in this work. The purpose of this would be to ascertain if one of them could be responsible for the presence of the slow reaction which begins at about

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(38) Loc. cit.

half hydrogenation of abietic acid as found in this work. This would possibly be of help in predicting the structure of the material which is responsible for the slow hydrogenation that occurs toward the end of the total hydrogenation of abietic acid as has been indicated.[1] It also might lead to a way of obtaining pure samples of this same material, since other routes to the formation of this chemical might not be complicated by the presence of other products, such as tetrahydroabietic acids.

Another value of this proposal would possibly result from the comparison of the relative rate constants of hydrogenation of these various so called dihydroabietic acids using the same conditions. This might be useful in showing that materials which are now considered to be different dihydroabietic acids are in reality the same compounds.

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[1] See above, page 42.

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VITA

VITA

Ronald G. Jones, the son of Mr. and Mrs. Preston F. Jones, was born November 29, 1933 in Yorkville, Georgia. He attended public elementary schools in Yorkville, Fairmount, and Powder Springs, Georgia. His high school education was completed in June, 1951 at Powder Springs High School. Concurrent with his attendance at the Atlanta Division, University of Georgia, from September 1951 through June 1953, he was employed by Southern Latex Corporation, Austell, Georgia, as a technician in the development laboratory. In September, 1953, he received a National Methodist Scholarship for continuation of his education at Emory University, where he was graduated with a B.A. degree in Chemistry in June, 1955. He was enrolled in the Graduate School, Emory University from September 1955 through August 1956 and was granted the M.S. Degree in Chemistry in 1957. In September 1956, he enrolled in the Graduate Division, Georgia Institute of Technology. He held research fellowships provided by the Georgia Institute of Technology Engineering Experiment Station from June 1957 through August 1959, and the Rayonier Fellowship from January through August of 1960.

He was married to Sara Eugenia Sanford in July of 1957 and in November of 1960 accepted a teaching position as Assistant Professor of Chemistry, Georgia State College of Business Administration, Atlanta, Georgia. He is a member of the American Chemical Society and of Sigma Xi.